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[Contributions from the Sheffield Laboratory of Yale University]

CXCV.—RESEARCHES ON PYRIMIDINES THE CONDENSATION OF UREA AND GUANIDINE WITH ESTERS OF ALLYLMALONIC AND SOME ALKYL-SUBSTITUTED ALLYLMALONIC ACIDS

[FIFTY-FOURTH PAPER]

BY TREAT B. JOHNSON AND ARTHUR J. HILL

It was stated in a previous paper[1] that a derivative of allylmalonic acid,

$$CH_2 : CHCH_2CH(COOH)_2,$$

in which the carboxyl groups are linked in such a manner as to prevent lactone formation after the addition of halogens or halogen acids to the ethylene bond, would be of value for synthetical purposes. With the object in view of preparing a compound of this character, we investigated the action of diethyl allylmalonate on thiourea. Instead of reacting normally, as we expected, to form allylthiobarbituric acid (I), the thiourea combined with this ester in a unique manner, giving the first representative of a new class of cyclic compounds, viz., μ-amino-α-keto-β-carbethoxy-δ-methyltetrahydro-

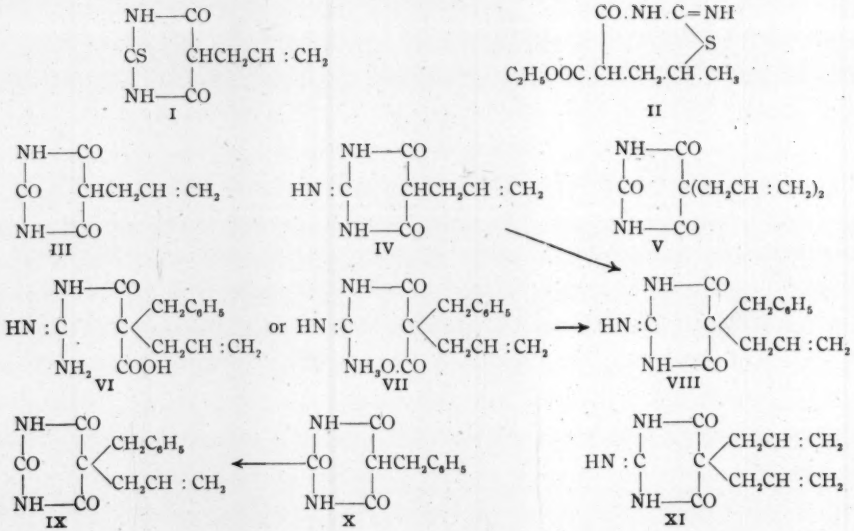
[1] Johnson and Hill: THIS JOURNAL, 45, 356 (1911).

hexathiazole (II). On the other hand, alkyl derivatives of diethyl allylmalonate—diethyl diallylmalonate and diethyl benzylallylmalonate—reacted in an entirely different manner and combined with thiourea, in the presence of sodium ethylate, forming, apparently, γ-lactone thioureas.

Because of this abnormal behavior of thiourea towards allylmalonates, it was therefore of interest to determine whether barbituric acid derivatives are formed by condensation of these same esters with urea and guanidine. We now find that urea condenses normally with diethyl allylmalonate, diethyl diallylmalonate and diethyl benzylallylmalonate, in the presence of sodium ethylate, forming smoothly allylbarbituric (III), diallylbarbituric (V) and benzylallylbarbituric (IX) acids, respectively. Allylbarbituric (III) and diallylbarbituric (V) acids were hydrolyzed smoothly, when heated with potassium hydroxide, giving the alkali salts of allylmalonic and diallylmalonic acids. On the other hand, all attempts to hydrolyze benzylallylbarbituric acid (IX) smoothly under the same conditions were unsuccessful. We also experienced this same difficulty when we attempted to hydrolyze benzylallylmalonylguanidine (VIII). Pure allylbenzylmalonic acid was not obtained in either case and the product of hydrolysis was an oil of indefinite composition. The structure of this pyrimidine (IX) was established by the fact that the same compound was formed by the action of allyl iodide on the silver salt of benzylbarbituric acid (X).[1]

Guanidine condensed normally with diethyl allylmalonate and diethyl diallylmalonate, in alcohol solution and in the presence of sodium ethylate, giving allylmalonylguanidine (IV) and diallylmalonylguanidine (XI), respectively. Both of these pyrimidines underwent hydrolysis smoothly, when heated with potassium hydroxide, giving allylmalonic and diallylmalonic acids, respectively (potassium salts). Diethyl benzylallylmalonate, on the other hand, condensed with guanidine, forming allylbenzyliminomalonuric acid (VI) or, which is more probable, its inner cyclic salt (VII). This latter structure (VII) is supported by the fact that the con-

[1] Conrad and Guthzeit: Ber. d. chem. Ges., **18**, 2846.

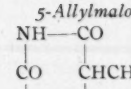

NH—CO
CS CHCH2CH : CH2
NH—CO
I
CO.NH.C=NH
S
C2H5OOC.CH.CH2.CH.CH3
II
NH—CO
CO CHCH2CH : CH2
NH—CO
III
NH—CO
HN : C CHCH2CH : CH2
NH—CO
IV
NH—CO
CO C(CH2CH : CH2)2
NH—CO
V
NH—CO
HN : C C CH2C6H5
CH2CH : CH2
NH2 COOH
VI
or
NH—CO
HN : C C CH2C6H5
CH2CH : CH2
NH2O.CO
VII
HN : C
VIII
NH—CO
CO C CH2C6H5
CH2CH : CH2
NH—CO
IX
NH—CO
CO CHCH2C6H5
NH—CO
X
HN : C
CH2CH : CH2
CH2CH : CH2
XI

densation product has no melting point below 300°, while an iminomalonuric acid would be expected to evolve carbon dioxide on heating and be converted into an acylguanidine. The corresponding dialkylmalonuric acids which have been examined all behave in this manner, when heated, and are transformed into acylureas.[1]

The iminomalonuric acid or the cyclic salt(?) is unstable in the presence of acids. When it was suspended in an excess of cold dilute hydrochloric acid it was immediately transformed into the hydrochloride of benzylallylmalonylguanidine (VII). This salt is dissociated by water and converted into the free base (VII), melting above 300°. The constitution of this pyrimidine was established by the fact that the same compound was formed by the action of benzyl iodide on the silver salt of allylmalonylguanidine (IV). Therefore the silver salts of benzylbarbituric acid and allylmalonylguanidine react with alkyl halides in a similar manner, and the alkyl radicals attach themselves to the carbon atom in the 5-position of the pyrimidine ring.

The study of allylpyrimidines will be continued.

EXPERIMENTAL PART

5-Allylmalonylurea (Allylbarbituric Acid),  .—Three and six-tenths grams of sodium were dissolved in 40 cc. of absolute alcohol and 4.5 grams of urea then dissolved in the solution. One molecular proportion of diethyl malonate (15 grams) was then poured into the solution and the mixture shaken vigorously, when a magma of a colorless sodium salt was formed immediately. This was heated at 100° for 5 hours to complete the reaction and the alcohol then expelled by heating on the steam bath. The sodium salt was dissolved in the least possible quantity of cold water, and dilute sulphuric acid added in slight excess. This pyrimidine separated in flesh-colored crystals. It was

[1] Fischer and Dilthey: Ann. Chem. (Liebig), **335**, 334 (1904).

purified by crystallization from hot, absolute alcohol and separated, on cooling, in almost colorless plates which melted at 167° to an oil without effervescence. The pyrimidine is soluble in boiling water and insoluble in benzene. The yield of purified material was 10.0 grams. Analysis (Kjeldahl):

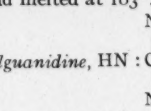
	Calculated for $C_7H_{10}O_3N_2$	Found I	Found II
N	16.66	16.72	16.72

Hydrolysis of Allylbarbituric Acid with Potassium Hydroxide. —Two grams of the barbituric acid were hydrolyzed by dissolving in 8.0 cc. of a 50 per cent. potassium hydroxide solution and then heating for 2 hours at 130°–150°. After acidifying with hydrochloric acid the solution was then evaporated at 100° to remove water and the residue triturated with warm absolute alcohol to dissolve the allylmalonic acid. On cooling, this acid separated. In order to identify it, it was dissolved in dilute sodium hydroxide solution and calcium chloride added, when its characteristic calcium salt separated. Calcium determination:

0.2457 gram substance gave 0.0761 gram CaO.

	Calculated for $C_6H_8O_4Ca$	Found
Ca	21.98	22.14

Some of this calcium salt was warmed in dilute hydrochloric acid solution. After cooling, the solution was then extracted with ether and the ether evaporated. We obtained in this manner the pure allylmalonic acid, which crystallized from benzene and melted at 103°.

5-Allylmalonylguanidine,  . —This pyrimidine was prepared by dissolving three molecular proportions of sodium (3 grams) in 45 cc. of absolute alcohol and adding to this solution 4.0 grams of guanidine hydrochloride and 8.0 grams of diethyl malonate. An immediate reaction took place with separation of a colorless sodium salt.

After heating for 5 hours to complete the reaction the excess of alcohol was then removed by evaporation at 100°. The salt was dissolved in a little cold water and sulphuric acid added in only slight excess, when this pyrimidine separated in beautiful pink prisms. It crystallizes from acetic acid in characteristic hexagonal tables which melt at 265°–266°. The compound is insoluble in alcohol and benzene but soluble in water. It contains two molecules of water of crystallization, which it loses when heated at 120°. Water determination:

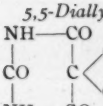
0.8600 gram substance lost 0.1441 gram H_2O.

	Calculated for $C_7H_9O_2N_3.2H_2O$	Found
H_2O	17.73	16.76

Nitrogen determination (Kjeldahl):

	Calculated for $C_7H_9O_2N_3.2H_2O$	Found	
		I	II
N	20.69	20.56	20.56

5,5-Diallylmalonylurea (Diallylbarbituric Acid),



—This pyrimidine was prepared by condensation of urea (2.4 grams) with diethyl diallylmalonate (10 grams) in the same manner as described in the preceding condensation. The yield was 8.0 grams. It crystallizes from 50 per cent. alcohol in characteristic, rhombohedral crystals which melt at 173° to a clear oil. The crystals are colorless. The pyrimidine is very soluble in cold alcohol and in warm water, but only moderately soluble in benzene. Nitrogen determinations (Kjeldahl):

	Calculated for $C_{10}H_{12}O_2N_2$	Found	
		I	II
N	13.46	13.26	13.26

Hydrolysis of Diallylbarbituric Acid with Potassium Hydroxide.—This pyrimidine was saponified by dissolving it (3 grams) in 50 per cent. potassium hydroxide solution (10 cc.)

and then heating for 4 hours at 145°. After heating, in an open dish, at 100° to remove ammonia the solution was cooled to 0°, acidified with hydrochloric acid, and finally extracted with ether. The ether solution was washed with water to remove hydrochloric acid, dried over sodium sulphate and the ether evaporated, when we obtained an oily product which immediately crystallized on cooling. This substance was chiefly diallylmalonic acid, but contaminated with some material which was not identified. When this mixture was dissolved in dilute ammonia and an excess of silver nitrate solution added the colorless, granular silver salt of diallylmalonic acid separated. After washing with water, alcohol, and finally with ether, it was dried for analysis in a desiccator over concentrated sulphuric acid. Silver determinations:

I. 0.1700 gram substance gave 0.0915 gram Ag.
II. 0.2500 gram substance gave 0.1347 gram Ag.

	Calculated for $C_9H_{10}O_4Ag_2$	Found I	Found II
Ag	54.27	53.82	53.80

5,5-Diallylmalonylguanidine, HN :C(NH—CO)(CO—NH)C(CH$_2$CH :CH$_2$)(CH$_2$CH :CH$_2$).—This was prepared by condensation of guanidine (9 grams of the hydrochloride) with diethyl diallylmalonate (22.7 grams) in the presence of sodium ethylate. The yield of the crude pyrimidine was 18.0 grams. It is soluble in acetic acid and insoluble in water and alcohol. It crystallizes from acetic acid in characteristic, colorless, rhombohedral prisms which do not melt below 300°. We experienced great difficulty in obtaining consistent results by the Kjeldahl method, therefore the nitrogen was determined by combustion (Dumas):

	Calculated for $C_{10}H_{12}O_2N_2$	Found
N	20.29	20.36

Hydrolysis of 5,5-Diallylmalonylguanidine with Potassium Hydroxide.—This pyrimidine was hydrolyzed under similar

conditions as those employed in the hydrolysis of 5,5-diallylbarbituric acid. After acidifying with hydrochloric acid the diallylmalonic acid was extracted with ether. It was obtained in colorless crystals after evaporation of the ether and melted at 133°.

5,5-Allylbenzylmalonylurea (*5-Allyl-5-benzylbarbituric Acid*), .—This was prepared by condensation of urea (1.4 grams) with diethyl allylbenzylmalonate (7 grams). The yield was 6 grams. The pyrimidine crystallizes from dilute alcohol in characteristic barrel-shaped prisms which melt at 198° to an oil. It is soluble in cold ether and absolute alcohol and insoluble in water. It did not contain water of crystallization. Nitrogen determinations after drying the pyrimidine at 100° (Kjeldahl):

	Calculated for $C_{14}H_{16}O_3N_2$	Found I	Found II
N	10.85	10.70	10.67

Hydrolysis of Allylbenzylbarbituric Acid with Potassium Hydroxide.—One and four-tenths grams of this pyrimidine were dissolved as usual in 10 cc. of 50 per cent. potassium hydroxide solution and heated for 3 hours at 135°. Ammonia was evolved, and also carbon dioxide on making the solution acid. The solution was acidified with hydrochloric acid and then thoroughly extracted with ether. The ether solution was washed with water, dried over sodium sulphate and the ether then evaporated, when we obtained a thick oil, having acid properties, which showed no signs of crystallizing on long standing. Assuming that we had in hand allylbenzylmalonic acid we therefore dissolved the product in a slight excess of dilute ammonia and then added silver nitrate in excess. A colorless, granular silver salt separated at once. It was washed with water, alcohol and ether and then dried for analysis in a desiccator over concentrated sulphuric acid. A silver determination on this salt gave a result lower than

the calculated value for a disilver salt of allylbenzylmalonic acid and indicated a mixture of this salt with the monosilver salt of the lactone[1] of this dibasic acid. Silver determination:

0.1076 gram substance gave 0.0400 gram Ag.

	Calculated for $C_{13}H_{12}O_4Ag_2$	Calculated for $C_{13}H_{13}O_4Ag$	Found
Ag	48.22	31.7	37.2

Because of this low result, we therefore repeated the hydrolysis twice under different conditions. We first heated with 50 per cent. alkali for 4 hours at 150° and in the second experiment for the same length of time at 170°, but even under these conditions we obtained an oily acid which would not crystallize on long standing. Furthermore, the analytical results for silver were higher than those obtained in the first experiment, but still were consistently much lower than the calculated value for a disilver salt. For example, we found 45.39, 45.14, 45.55 and 45.58 per cent. of silver, while the calculated value is 48.22.

Since this compound did not undergo hydrolysis smoothly, giving the corresponding malonic acid, as observed in the two previous cases, we therefore established its structure by its synthesis in another manner. For example: Ten and five-tenths grams of benzylbarbituric acid[2] and 2.9 grams of potassium hydroxide were dissolved in warm water and mixed with an aqueous solution of silver nitrate (9.4 grams of the salt). The silver salt of the pyrimidine deposited at once. This was separated by filtration, washed with water, alcohol and ether and then thoroughly dried in a desiccator over sulphuric acid. This dry salt was then suspended in anhydrous ether and digested with a molecular proportion of allyl iodide for 8–9 hours. Silver iodide was formed. The ether solution was then filtered and the ether allowed to evaporate, when a solid substance was obtained. This was dried on a porous plate to remove traces of allyl iodide and finally washed with ether. The compound crystallized from dilute alcohol in the charac-

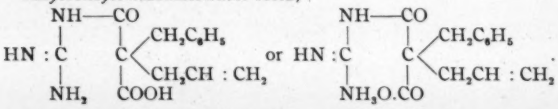
[1] Johnson and Hill: *Loc. cit.*

[2] Conrad: *Loc. cit.*

teristic, barrel-shaped prisms of allylbenzylbarbituric acid and melted at 197°. A mixture of this compound and the barbituric acid derivative melted at 197°–198°. The allyl group therefore entered the 5-position of the pyrimidine ring. An attempt to alkylate this pyrimidine by digestion of the silver salt in absolute alcohol with pure distilled allyl iodide was unsuccessful. Hydriodic acid apparently was generated, under these conditions, and decomposed the salt, forming silver iodide and the unaltered benzylbarbituric acid.

Condensation of Diethyl Allylbenzylmalonate with Guanidine

Allylbenzylimidomalonuric Acid,



—One and sixty-five hundredths grams of sodium were dissolved in 50 cc. of absolute alcohol and 2.37 grams of finely pulverized guanidine hydrochloride sifted into the solution. Seven and two-tenths grams of diethyl allylbenzylmalonate were then added and the mixture warmed gently at 100°, when a colorless sodium salt separated. The heating was continued for 5 hours and the excess of alcohol then removed. This compound was obtained by dissolving the salt in water and then adding a slight excess of sulphuric acid. It crystallizes from acetic acid in needlelike prisms which do not melt below 300°. The compound is insoluble in ether, alcohol, water and benzene. The yield was 9 grams. Analyses (Kjeldahl):

	Calculated for $C_{14}H_{17}O_3N_3$	Found I	II	III	IV	V
N	15.7	15.3	15.32	15.65	15.67	15.65

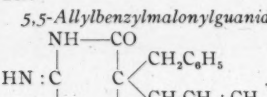
This interesting compound is especially characterized by its behavior towards hydrochloric acid. Seven-tenths of a gram of the compound, finely pulverized, was placed in a dry test tube and 5 cc. of cold dilute hydrochloric acid poured

upon the dry powder. The compound began to undergo a change immediately at ordinary temperature. It first melted and deposited on the bottom of the test tube as a thick gum. There was no apparent evolution of heat during this transformation. This oily product finally completely solidified, forming beautiful prismatic crystals. After being allowed to stand in the acid for about 5 minutes it was filtered off and without further treatment placed in a desiccator over sulphuric acid and potassium hydroxide and allowed to dry. This substance gave a strong test for chlorine and a nitrogen determination (Kjeldahl) indicated a basic salt of allylbenzylmalonylguanidine:

	Calculated for $(C_{14}H_{15}O_2N_4)_2HCl$	Found
N	15.20	15.03

This salt is completely dissociated by water. When warmed with water, the solution gave a strong test for free hydrochloric acid and the pyrimidine separated as a colorless powder.

5,5-Allylbenzylmalonylguanidine,



.—This same pyrimidine was also obtained by alkylation of 5-allylmalonylguanidine with benzyl iodide. For example: Allylmalonylguanidine was dissolved in water containing one molecular proportion of potassium hydroxide and the silver salt precipitated by addition of the required amount of silver nitrate solution. This was filtered off, washed free from inorganic salts with water and alcohol and then dried in a desiccator over sulphuric acid. Twelve grams of this dry silver salt were suspended in 50 cc. of dry ether and digested, on the water bath, with 9.9 grams of benzyl iodide. Silver iodide began to form almost immediately and after 5 hours' digestion the reaction was complete. The pyrimidine separated with the silver iodide and when the ether was evaporated only a small amount of unaltered benzyl iodide was obtained. In order to obtain the

pyrimidine the mixture of silver iodide and pyrimidine was digested with acetic acid and the solution filtered and cooled. The pyrimidine then separated as a fine, colorless powder which did not melt below 300°. It was absolutely identical with the product formed by the action of hydrochloric acid on allylbenzyliminomalonuric acid. The pyrimidine is insoluble in water and alcohol. Nitrogen determinations (Kjeldahl):

	Calculated for $C_{14}H_{18}O_2N_2$	Found I	Found II
N	16.34	16.1	16.6

Hydrolysis of Allylbenzylmalonylguanidine with Potassium Hydroxide.—As in the case of allylbenzylbarbituric acid, attempts to obtain pure allylbenzylmalonic acid by hydrolysis of this malonylguanidine, with alkali, were unsuccessful. Two grams of the pyrimidine were dissolved in 6 cc. of 50 per cent. potassium hydroxide solution and heated for 2.5 hours at 130°. The acid was separated as in the hydrolysis of allylbenzylbarbituric acid, and was obtained as an oil which would not crystallize. A silver salt was made in the usual manner and the following result obtained for silver:

	Calculated for $C_{13}H_{17}O_4Ag_2$	Found
Ag	48.22	38.48

Several attempts were then made to obtain a definite acid by heating the pyrimidine with 50 per cent. alkali from 2 to 5 hours at 150°. In every case we failed to obtain a silver salt that contained over 43 per cent. of silver. The results of six different determinations on salts prepared after various hydrolyses are as follows:

	Calculated for $C_{13}H_{17}O_4Ag_2$	Found I	II	III	IV	V	VI
Ag	48.22	42.56	42.66	41.16	41.03	42.70	42.83

Allylbenzylmalonic Acid, $CH_2 : CHCH_2 \diagdown C(COOH)_2$ $C_6H_5CH_2 \diagup$.—This was prepared by dissolving 2 grams of its ethyl ester and 3 molecular proportions of potassium hydroxide (2.7 grams)

in 50 per cent. alcohol and heating the solution for 14 hours on the steam bath. After cooling, hydrochloric acid was added in excess and the acid solution repeatedly extracted with ether to remove the malonic acid. After evaporating the excess of ether the acid was obtained as a thick oil which did not crystallize. It was dissolved in dilute ammonia and the silver salt prepared by addition of silver nitrate solution. It separated in a granular condition and, after being washed with water, alcohol and ether, was dried for analysis in a desiccator over sulphuric acid. Silver determination:

0.3310 gram substance gave on ignition 0.1580 gram Ag.

	Calculated for $C_{13}H_{12}O_4Ag_2$	Found
Ag	48.22	47.74

NEW HAVEN, CONN.
August 11, 1911

[Contributions from the Chemical Laboratory of Harvard University]

1,3,5 - TRIIOD - 2 - BROM - 4,6 - DINITROBENZENE AND SOME OF ITS DERIVATIVES[1]

BY C. LORING JACKSON AND H. E. BIGELOW

In 1888, W. S. Robinson and one of us[2] found that sodic malonic ester converted tribromdinitrobenzene, $C_6HBr_3(NO_2)_2$, into bromdinitrophenylmalonic ester,

$$C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2,$$

by the replacement of one atom of bromine by hydrogen and another by the malonic ester residue. The further investigation of this subject brought to light many similar cases of replacement of halogens by hydrogen, and in the present paper we describe our study of 1,3,5-triiod-2-brom-4,6-dinitrobenzene, $C_6I_3Br(NO_2)_2$, which, when treated with sodic malonic ester in the cold, is converted into the compound

$$C_6HI_2Br(NO_2)_2$$

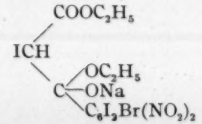
[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Harold E. Bigelow.

[2] THIS JOURNAL, **11**, 93 (1889).

with acetylenetetracarbonic ester, $C_2H_2(COOC_2H_5)_4$, as the secondary product; while, if the reaction is carried on hot, the substituted malonic ester, $C_6HIBr(NO_2)_2CH(COOC_2H_5)_2$, is formed. This discovery proves the incorrectness of the reactions[1] by which the formation of the acetylenetetracarbonic ester has been explained hitherto, since these are impossible without free malonic ester, which was excluded from these experiments by the use of a slight excess of sodic ethylate and could not have been set free from sodic malonic ester, as in the earlier reactions, because no acid substance was present. It became necessary therefore to explain the formation from sodic malonic ester of iodmalonic ester (the mother substance of the acetylenetetracarbonic ester), and the only hypothesis we have found for this consists in assuming that the sodic malonic ester reacts in the enol form,

$$CH = (CONaOC_2H_5)—(COOC_2H_5),$$

and that the action consists in the addition of the I and $—C_6I_2Br(NO_2)_2$ radicals at the double bond, when the more acid of these will undoubtedly attach itself to the carbon carrying the ONa group, and this may well be the substituted phenyl loaded with the highly negative nitro groups and halogens. In that case we shall have the compound



On acidification the hydrogen of the hydroxyl might combine with the substituted phenyl, giving the compounds

$$C_6HI_2Br(NO_2)_2 \text{ and } CHI(COOC_2H_5)_2,$$

which, reacting with the excess of sodic malonic ester, will give acetylenetetracarbonic ester, the two products actually obtained. This hypothesis not only explains the formation of the acetylenetetracarbonic ester, but also gives the first

[1] Jackson and Moore: THIS JOURNAL, **12**, 7. Jackson: *Ibid.*, 307 (1890).

explanation of the replacement of a halogen by hydrogen under these conditions.

Of the suppositions which make up this hypothesis, perhaps the least probable is the splitting off of the $-C_6I_2Br(NO_2)_2$ group with the hydrogen of the hydroxyl, as this necessitates breaking apart two atoms of carbon, one of which forms part of a benzene ring. Some reasons have occurred to us for believing such an action might take place, but we think it unwise to discuss these, or other arguments in favor of our hypothesis, before it has been brought to the test of experiment by work now in progress in this laboratory.

If this hypothesis should be accepted it will also explain the similar behavior with acetacetic ester, but we do not see how it can be applied to the replacements of halogen by hydrogen under the influence of sodic alcoholates, unless it is assumed that the intermediate addition compounds in these cases contain quadrivalent oxygen, and are therefore analogous to the quinhydrones as formulated by Richter.[1]

The work described in this paper, with that also on compounds of iodine by Langmaid and one of us,[2] has established the order of the halogens in regard to replacement by hydrogen rather than by the malonic ester radical as follows: Chlorine has the least tendency of this sort, since only one case[3] of it has been observed, so far as we know; bromine undergoes the replacement by hydrogen as easily as that by the malonic ester residue, and iodine with more ease; so that the tendency toward the hydrogen substitution increases as the acidity of the element decreases, which is a strong argument in favor of our hypothesis.

In preparing 1,3,5-triiod-2-brom-4,6-dinitrobenzene,

$$C_6I_3Br(NO_2)_2,$$

it was found that a persistent impurity of triioddibromnitrobenzene was formed, if the triiodaniline used contained the dark-colored substances with which it is usually contaminated, and further, that these are produced either by an excess

[1] Ber. d. chem. Ges., **43**, 3603 (1910).
[2] This Journal, **32**, 304 (1904).
[3] Jackson and Gazzolo: *Ibid.*, **22**, 51 (1899).

of iodine, or by trichloride of iodine in the chloride of iodine. By making this substance with sufficient chlorine to give a slight amount of trichloride of iodine, and then decomposing this by heat, a product was obtained which gave a nearly colorless triiodaniline when passed into a solution of aniline hydrochloride; and from this the pure 1,3,5-triiod-2-brom-4,6-dinitrobenzene melting at 292° was obtained without difficulty.

The impurity formed, when dark-colored triiodaniline was used, gave percentages of halogen agreeing with the formula $C_6I_3Br_2NO_2$, but this must be accepted with some reserve, as it is not supported by analyses for carbon and nitrogen, which were impossible with the amount of pure material at our disposal after the extended fractional crystallization necessary to obtain it. The 1,3,5-triiod-2,4-dibrom-6-nitrobenzene melts at 255° to 256° with blackening, but melting points as high as 260° have been observed. We ascribe these differences to variations in the conditions under which the decomposition point was observed; in fact, much greater differences than this have been found in similar cases in this laboratory. It is almost impossible to separate this substance completely from the dinitro compound by crystallization, so a better way to obtain it is to treat the mixture with sodic malonic ester, which acts on the dinitro but not on the mononitro compound, after which this latter can be more easily separated from the other products by fractional crystallization. This greater inertness of the mononitro compound is another example of the slighter influence of an atom of bromine than of a nitro group on halogen atoms ortho-para to it. The triiod-dibromnitrobenzene was probably formed during the boiling with fuming nitric acid by the destruction of a portion of the dark impurity of the triiodbrombenzene, giving free bromine which then replaced one atom of hydrogen in that substance, the nitric acid subsequently converting it into the nitro compound. The iodine also formed by this decomposition was converted into iodic acid, which was always obtained in such preparations. The formation of tetrabromdinitrobenzene from

tribromdinitrobenzene,[1] and of pentabromnitrobenzene from tetrabrombenzene[2] with nitric acid are parallel cases.

The 1,3,5-triiod-2-brom-4,6-dinitrobenzene, when treated with sodic malonic ester, gave, as already stated, in the cold, or when heated for a short time, the 1,3-diiod-2-brom-4,6-dinitrobenzene, $C_6HI_2Br(NO_2)_2$, melting at 187°, and in addition to this acetylenetetracarbonic ester, $C_2H_2(COOC_2H_5)_4$, which would be expected[3] as the secondary product from such a replacement of halogen by hydrogen. If instead the sodic malonic ester was heated for some time with the dinitro compound, the reaction went further, forming the 1-iod-2-brom-4,6-dinitrophenyl-3-malonic ester,

$$C_6HIBr(NO_2)_2CH(COOC_2H_5)_2,$$

melting at 107°. This agrees with the only other case known of this reaction with an iodine compound, as the 1,3,5-triiod-dinitrobenzene[4] gave with sodic malonic ester diioddinitrobenzene with but little ioddinitrophenylmalonic ester. The constitution of these substances has not been determined experimentally, but analogy with the corresponding bromine compounds[5] leaves no doubt that their structure is that given above.

The observation that one atom of iodine is replaced by hydrogen *before* any iodine has beeen replaced by the malonic ester radical was rendered possible by the fact that iodine shows a greater tendency toward the hydrogen substitution than toward that by the malonic ester radical, while with the bromine compounds the halogen seems to be replaced with equal ease by hydrogen or by the malonic ester radical, so that the action could not be stopped after it had run half way. On the other hand, the reaction with sodic alcoholates and tribromdinitrobenzene[6] ran in two stages, the first being the replacement of two atoms of bromine by two ethoxyls, followed by that of the third atom by hydrogen. As this was

[1] Jackson and Wing: THIS JOURNAL, **10,** 283 (1888).
[2] Jackson and Bancroft: *Ibid.*, **12,** 289 (1890).
[3] Jackson and Moore: *Ibid.*, **12,** 7 (1890).
[4] Jackson and Langmaid: *Ibid.*, **32,** 304 (1904).
[5] Jackson and Robinson: *Ibid.*, **11,** 557 (1889).
[6] Jackson and Warren: *Ibid.*, **13,** 164 (1892).

the only observation of the sort known before our present work, our opposite result was decidedly unexpected, and the new light shed on the subject by this discovery led to the hypothesis given at the beginning of this paper.

When sodic ethylate acted on tribromtrinitrobenzene (which is the true analogue of our bromdinitro substance), two different reactions took place simultaneously[1]—the replacement of all three atoms of bromine by ethoxyls, giving trinitrotriethoxybenzene, $C_6(OC_2H_5)_3(NO_2)_3$, and the replacement of two nitro groups by ethoxyls, giving tribromnitrodiethoxybenzene, $C_6Br_3NO_2(OC_2H_5)_2$; while the 1,2,3,5-tetrabromdinitrobenzene gave the replacement of the 2-bromine and a nitro group by ethoxyls.[2] It was not surprising therefore that our compound was converted into 1,3,5-triiod-2-brom-6-nitro-4-phenetole, melting at 148°, by sodic ethylate, and into the corresponding anisole melting at 163° by sodic methylate. It is probable that the parallel replacement of the iodine atoms also occurred to a limited extent, as the wash waters from the reaction product gave a test for halogen.

The effect of reducing agents on our 1,3,5-triiod-2-bromdinitrobenzene was also tried to see if the iodine could be removed by reagents which ordinarily do not produce this effect, since Calvert and one of us[3] had found that tin and hydrochloric acid converted tribromdinitrobenzene,

$$C_6HBr_3(NO_2)_2,$$

into metaphenylenediamine, while zinc and acetic acid gave tribromphenylenediamine. Our experiment with tin and hydrochloric acid gave no satisfactory result, and another with stannous chloride left our dinitro compound unaffected, which, however, we think was probably due to our failure to find the proper conditions; but we did not repeat these experiments, as zinc and acetic acid removed all three atoms of iodine, forming 2-brom-4,6-diaminobenzene, $C_6H_3Br(NH_2)_2$, melting at 92°, and, as this mixture had not removed the bromine in the earlier work, there was no question that the more

[1] Jackson and Warren: THIS JOURNAL, **15**, 607 (1894).
[2] Jackson and Calvert: *Ibid.*, **18**, 298 (1896).
[3] *Ibid.*, **18**, 467 (1896).

efficient tin and hydrochloric acid would produce the same effect, when the proper conditions were found. We next tried to find a reducing agent which would leave the iodine untouched. Sulphurous acid had no action, iron and acetic acid gave the symmetrical bromphenylenediamine, and so did the use of iron by hydrogen and sulphuretted hydrogen recommended by Merz and Weith[1]— a method which does not deserve the neglect into which it has fallen. These results made it probable that all acid agents would replace the iodine by hydrogen, and, as the usual alkaline reducer, ammonic sulphide with sulphuretted hydrogen, was inadmissible for fear of the formation of organic sulphides, we tried ferrous hydroxide, and with this obtained the 1,3,5-triiod-2-bromphenylenediamine, $C_6I_3Br(NH_2)_2$, which melts at 187°, and shows basic properties, but so reduced by the halogen atoms in the molecule that its hydrochloride,

$$C_6I_3BrNH_2NH_3Cl,$$

is decomposed at 100°.

The 1,3,5-triiod-2-brom-6-nitro-4-phenetole was converted by zinc and acetic acid into metaminophenol, recognized by the decomposition point of its hydrochloride, which we found to be 225°. Ikuta[2] gives 229°. In this case, therefore, the reduction was more complete than in that of the dinitro compound, as even the bromine has been removed, which seems to show that a hydroxyl or ethoxyl has greater loosening effect than an amino group. The loosening effect on the halogens is ascribed to the amino rather than the nitro groups, as it seems probable that the first action of the reducing agent would be exercised on the nitro groups, and the work of Calvert and one of us[3] has shown that amino groups produce such a loosening effect on halogens.

We have also tried reduction experiments on a number of related iodine compounds. Zinc and acetic acid remove iodine from 1,3,5-triioddinitrobenzene. The metaphenylenediamine was not isolated, but a quantitative determination showed

[1] Z. Chem., **1869**, 242.
[2] This Journal, **15**, 40.
[3] *Ibid.*, **18**, 467 (1896).

that in one case as much as 81 per cent. of the iodine had been removed. 1,3,5-Triiodaniline gave no removal of iodine with tin and hydrochloric acid, and a mere trace with zinc and acetic acid. The corresponding tribromaniline, on the other hand, is converted into dibromaniline in a few hours by tin and hydrochloric acid,[1] so that here we have a striking difference in the behavior of the two halogens, unless, indeed, it is due to a difference in the conditions of the experiments. 1,3,5-Triiod-2-brombenzene with zinc and acetic acid lost the two atoms of iodine ortho to the bromine, giving *p*-iodbrombenzene melting at 92°, the removal of the iodine in this case being much easier than would be expected. A quantitative determination of the amount of halogen eliminated showed that there was a secondary action, in which still more of it was replaced by hydrogen. The reduction experiments therefore confirm the inference drawn from those with sodic malonic ester, that iodine shows a greater tendency than bromine to be replaced by hydrogen, the only exception being the case of the triiodaniline compared with tribromaniline. In considering this inference it must be remembered that the conditions under which the experiments were tried, such as temperature, solvents, and others, were not necessarily parallel, since they were carried on by different men with an interval of several years, but we think that in spite of this there are enough agreeing observations to justify the conclusion to which we have come. Work in this direction will be continued in this laboratory.

Sodic ethylate did not act, so far as we could find, on 1,3,5-triiodbenzene, and only very slightly on 1,3,5-triiod-2-brombenzene, as but a trace of sodic halide could be found. The same reagent caused the substitution of bromine by hydrogen in 1,3,5-trichlor-2-brombenzene[2] with apparent ease, and with less ease in 1,2,3,5-tetrabrombenzene,[3] so, if these observations are confirmed by further experiments, chlorine in the 1,3,5 positions exerts the greatest loosening effect on a

[1] Jackson and Calvert: THIS JOURNAL, **18**, 468 (1896).
[2] Jackson and Gazzolo: *Ibid.*, **22**, 50 (1899).
[3] Jackson and Calvert: *Ibid.*, **18**, 298 (1896).

bromine atom on the benzene ring, bromine less, and iodine the least.

EXPERIMENTAL PART

In preparing triiodaniline by the method of Michael and Norton,[1] modified by Langmaid[2] and one of us and by Green[3] and one of us, we were troubled like our predecessors with the formation at first of a brown impure substance from which it was hard to obtain satisfactory derivatives. After many experiments we found that brown impurities were formed if the chloride of iodine used contained trichloride of iodine on the one hand, or an excess of iodine on the other, but that with pure chloride of iodine, made by the following process, a triiodaniline of excellent quality could be obtained with a yield often as high as 80 per cent. of the theoretical, and pure enough to be used directly in making bromtriiodbenzene. The 42 grams of iodine (to be used with 10 grams of aniline) were treated with a rapid stream of chlorine until yellow crystals of trichloride of iodine appeared on the sides of the flask, which must be shaken frequently during the process, as these yellow crystals may be formed while there is still much unaltered iodine in the bottom of the flask. The crystals formed at first usually dissolved on shaking, and the shaking, followed by addition of chlorine, was continued until the yellow crystals appeared at once on the addition of more chlorine. The flask was then covered with a watch glass and could be kept in a cool place even for some days. Just before using, the mixture was heated gently on the steam bath for about 10 minutes, with occasional shaking, and in this way the trichloride was decomposed, the chlorine escaped and the residue was monochloride of iodine pure enough for our purpose. It was heated to about 60° and passed by means of a current of air into a solution of 10 grams of freshly distilled aniline in 500 cc. of strong hydrochloric acid and 7 liters of water, as described in previous papers.

1,3,5-Triiod-2-brombenzene, $C_6H_2I_3Br$.—Ten grams of this

[1] Ber. d. chem. Ges., **21**, 1707 (1888).
[2] This Journal, **29**, 300 (1904).
[3] *Ibid.*, **31**, 600 (1906).

triiodaniline, mixed with 120 cc. of glacial acetic acid and 40 cc. of constant-boiling hydrobromic acid, were treated with two and a half grams of sodic nitrite, which was finely powdered and sifted into the flask in small quantities at a time, the flask being shaken thoroughly and cooled with running water after each addition. This took from one to four hours (the solid at no time having gone completely into solution), and after all the nitrite had been added, the mixture was allowed to stand overnight and then gently heated for a few minutes to start the decomposition of the diazo compound, when it was allowed to stand at ordinary temperature until the evolution of nitrogen had nearly ceased, after which the heating and standing were continued as long as any reaction was observed. If the triiodaniline was pure, yellow crystals were obtained, the yield being 22 grams from 20 grams of triiodaniline, that is, 93 per cent. of the theoretical. If, on the other hand, the dark brown triiodaniline was used, the diazo compound, on heating, either went into solution or changed to an oil which, on cooling, solidified to a black tarry mass, and from this very little triiodbrombenzene could be obtained. The products in this case will be discussed later. The yellow product was purified by recrystallization from alcohol until it showed the constant melting point 146°.

I. 0.1638 gram substance gave 0.2726 gram AgBr + AgI.[1]
II. 0.1481 gram substance gave 0.2467 gram AgBr + AgI.
III. 0.1776 gram substance gave 0.2952 gram AgBr + AgI.

	Calculated for $C_6H_2BrI_3$	Found I	Found II	Found III
BrI_3	86.16	85.90	85.96	85.76

The constitution of this triiodbrombenzene follows from its preparation from symmetrical triiodaniline.

Properties of 1,3,5-Triiod-2-brombenzene.—It crystallizes from alcohol in very light yellow needles and melts at 146°. It is easily soluble in ether, chloroform, acetone, benzene, toluene, carbonic disulfide, ethyl acetate, petroleum ether or amyl alcohol; slightly soluble in cold, soluble in hot ethyl

[1] The analyses were made by the method of Carius, and the halogens calculated on the assumption that the mixture was AgBr + 3AgI, which is justified by the method of formation of the substance.

alcohol; nearly insoluble in cold, soluble with difficulty in hot glacial acetic acid. Alcohol is the best solvent for it. Hydrochloric acid, nitric acid, sulphuric acid or sodic hydroxide is without action on it hot or cold.

As already mentioned, the product of the diazo reaction on a brown impure triiodaniline was a black or dark red tarry mass, from which a little triiodbrombenzene could be obtained by repeated crystallizations from benzene and chloroform, but we did not succeed in raising its melting point above 139°. This difference of 7° in melting point was apparently caused by a very small amount of impurity, as this specimen gave good results on analysis (I), but it is much easier to start from pure triiodaniline, as already advised. From the benzene and chloroform mother liquors of the first crystallization a nearly white substance melting at 82° was obtained, but in too small quantity for analysis, and we had no time to follow this line of work further.

1,3,5-Triiod-2-brom-4,6-dinitrobenzene, $C_6I_3Br(NO_2)_2$.—Triiodbrombenzene, melting not lower than 139°, was heated with fuming nitric acid of specific gravity 1.51 in a flask with a return condenser attached by a ground-glass joint. After heating for several hours there were crystals in the hot acid, more of which were deposited on cooling; the liquid was then poured off into water, giving an additional quantity of the product, all of which was washed with water, and crystallized from a mixture of equal parts of alcohol and benzene until it showed the constant melting point 292°, when it was dried at 100° for analysis. This product is obtained easily by heating with the acid for two or three hours, but, if crude triiodbrombenzene is used, the process runs less satisfactorily, in the way described after the properties of the dinitro compound.

I. 0.1084 gram substance gave 0.1555 gram AgI + AgBr.
II. 0.2011 gram substance gave 0.2862 gram AgI + AgBr.

	Calculated for $C_6I_3Br(NO_2)_2$	Found	
		I	II
Br + I	73.76	74.03	73.47

The method of preparation determines the constitution of the substance.

Properties of 1,3,5-Triiod-2-brom-4,6-dinitrobenzene.—It forms white needles sometimes a centimeter in length and melts at 292°. Freely soluble in acetone; somewhat soluble in cold, freely in hot benzene or chloroform; nearly insoluble in cold, not very soluble in hot alcohol; essentially insoluble in cold, somewhat more soluble in hot ether or tetrachloride of carbon; only slightly soluble in glacial acetic acid, even when hot. Aniline dissolves it easily without change of color. Not acted on by hydrochloric acid, nitric acid, sulphuric acid or a solution of sodic hydroxide even when hot.

In most of our preparations of the dinitro compound crude triiodbrombenzene was used, when it was found wise to carry on the heating for 24 hours, and if the melting point of the product was low, which happened not infrequently, to crystallize from alcohol and benzene and boil again with fuming nitric acid. We have devoted much time to the study of the impurity formed under these conditions but without entirely satisfactory results, so that all our statements on this subject must be regarded as preliminary. The principal secondary product from the action of boiling fuming nitric acid on triiodbrombenzene crystallized sometimes in short hexagonal prisms, at others in needles, and melted somewhat indefinitely at 256°, although melting points as high as 260° have been observed. As the melting was accompanied by blackening, these differences may be due to the fact that it is a decomposition point, not a true melting point, rather than to the presence of impurities. The substance had been crystallized repeatedly before the melting point was taken. This same substance, to judge from crystalline form, melting point and solubility, was obtained when crude triiodbromdinitrobenzene was heated with sodic malonic ester. Analysis I was made with a specimen direct from nitric acid, II, III and IV with specimens from the malonic ester reaction.

I. 0.1032 gram substance gave 0.1696 gram AgBr + AgI.

II. 0.1779 gram substance gave 0.2929 gram AgBr + AgI.

III. 0.1194 gram substance gave 0.1968 gram AgBr + AgI.

IV. 0.2424 gram substance gave, on combustion, 0.1019 gram CO_2.

	Calculated for $C_6Br_2I_3(NO_2)$	Found I	II	III	IV
Br + I	82.28	82.29	82.46	82.53	...
C	10.93	...	...	...	11.46

In spite of the variation in melting points, these results seem to determine the nature of the substance, if, as is fair to suppose, the numerous crystallizations have removed impurities. The formation of a substance of this sort is not unexpected, as shown in the introduction.

Properties of Triioddibromnitrobenzene, $C_6I_3Br_2NO_2$.—It forms white crystals, at times short hexagonal prisms, at others needles. It melts with blackening at 256°, but could be made to blacken as low as 253° and to melt as high as 260° under different conditions. It is very soluble in ether, acetone, chloroform, ethyl acetate, benzene or toluene; nearly insoluble in cold, soluble in hot methyl alcohol or glacial acetic acid; soluble with difficulty in ethyl alcohol. The substance prepared directly from nitric acid was found to be insoluble in ligroin, while that extracted in the malonic ester reaction was soluble; this is the only difference in solubility observed by us, and we ascribe it to a difference in the boiling point of the ligroin used in the two cases, since quite as marked a difference was found in the solubility of iodbromdinitrophenylmalonic ester when it was treated with low-boiling or high-boiling ligroir. The strong acids or a solution of sodic hydroxide have no effect on it, even if hot. Sodic malonic ester seems to be without action on it.

It may be worth mention that a product from the fractional crystallization of the mixture formed by the action of boiling nitric acid on crude triiodbrombenzene gave results on analysis agreeing fairly well with the formula $C_6HI_3BrNO_2$ (calculated, Br + I, 79.89; found, 78.47, 78.16), but we do not feel inclined to accept these results, as the melting point, 258°-260°, was not sharp and lies very near that of the dibrom compound just described, and the substance did not give triiodbromdinitrobenzene by further treatment with fuming nitric acid. Iodic acid was also found among the secondary products.

1,3,5-Triiod-2-brom-4,6-dinitrobenzene and Sodic Malonic Ester Action in the Cold

Ten grams of the triiodbromdinitrobenzene were dissolved in benzene dried by long standing with sodium and mixed with a solution of sodic malonic ester made from 1.5 grams of sodium, 50 grams of absolute alcohol and 10.6 grams of malonic ester, which amounts to 4 molecules of the ester for each molecule of the substituted benzene. A claret color appeared as soon as the solutions were mixed. After standing at ordinary temperatures for three or four hours the mixture was poured into highly diluted sulphuric acid and shaken thoroughly. The benzene, which held most of the color, was separated from the aqueous portion, and this at first was extracted with ether but, as the extract was only a very little oil, which did not solidify after standing for a year, this treatment was abandoned in later experiments. The principal amount of the products was contained in the benzene solution, which was allowed to evaporate spontaneously, when it left a solid mixed with a considerable amount of a dark red oil. After removing the oil by pressing between filter papers the residue was crystallized from alcohol and in this way two substances were isolated, one slightly yellowish and melting at 187°, the other white and melting at 75°.

1,3-Diiod-2-brom-4,6-dinitrobenzene, $C_6HI_2Br(NO_2)_2$.—The substance melting at 187° was dried at 100°.

I. 0.1981 gram substance gave 0.2608 gram AgI + AgBr.

II. 0.1733 gram substance gave 0.2297 gram AgI + AgBr.

III. 0.1961 gram substance gave 10.20 cc. N_2 at 28° and 758.5 mm.

	Calculated for $C_6HI_2Br(NO_2)_2$	Found I	II	III
Br + I_2	66.92	66.82	67.31	...
N	5.61	...	...	5.69

The compound was formed therefore by the replacement of one atom of iodine by one of hydrogen. The position of this iodine has not been determined experimentally, but the analogy of the bromine compounds leaves little doubt that it is the one between the two nitro groups.

Properties of 1,3-Diiod-2-brom-4,6-dinitrobenzene.—It forms straw-colored needles, often half a centimeter in length, with abrupt terminations. It melts at 187°. It is easily soluble in methyl alcohol, ether, acetone, chlorofrom, ethyl acetate, benzene or toluene; easily soluble in hot alcohol, nearly insoluble in cold; slightly soluble in hot ligroin, essentially insoluble in it when cold. Alcohol is the best solvent for it, but good results can also be obtained from a mixture of benzene and ligroin. When this substance, dissolved in dry benzene, was heated with sodic malonic ester, it was converted into the iodbromdinitrophenylmalonic ester described later, which was recognized by its melting point.

Acetylenetetracarbonic Ester

The substance melting at 75°, obtained by the action of triiodbromdinitrobenzene and sodic malonic ester in the cold, was easily separated from the diiod compound by crystallization from alcohol, in which it is more soluble. Its melting point, 75° instead of 76°, and the fact that it contained no nitrogen suggested that it was the acetylenetetracarbonic ester, which was confirmed by the following analysis:

	Calculated for $C_2H_2(COOC_2H_5)_4$	Found
C	52.83	53.33
H	0.69	0.58

This ester is the secondary product to be expected in all cases where a halogen is replaced by hydrogen by means of sodic malonic ester.[1] It was detected in all our experiments where such a replacement had occurred.

1,3,5-Triiod-2-brom-4,6-dinitrobenzene and Sodic Malonic Ester Action when Heated

When the reaction mixture was heated for only half an hour, the same products were obtained as in the cold, that is, diiodbromdinitrobenzene and acetylenetetracarbonic ester, with occasionally a small amount of a substance melting near 260°. Accordingly, the heating was carried on for twelve

[1] THIS JOURNAL, **12**, 308 (1890).

hours on the steam bath in a flask with a return condenser, after which the product was poured into diluted sulphuric acid, thoroughly shaken, and the layer of benzene removed and allowed to evaporate spontaneously. The residue sometimes crystallized at once, at others it was an oil which required standing for days or even months before it solidified. The solid was divided by crystallization from alcohol into two products (in addition to acetylenetetracarbonic ester), one of which was the substituted malonic ester described below, while the other melted at 256° and proved to be the triiodd-ibromnitrobenzene already obtained by the action of nitric acid on impure triiodbrombenzene and described earlier in this paper. Its appearance here may be explained by the supposition that the triiodbromdinitrobenzene mixed with it had reacted to form the substance about to be described, which could then be separated from the more inert dibromnitro compound by crystallization.

1-Iod-2-brom-4,6-dinitrophenyl-3-malonic Ester, $C_6HIBr(NO_2)_2CH(COOC_2H_5)_2$.—This substance was obtained from the oily product of the reaction of sodic malonic ester on triiodbromdinitrobenzene which was drained away from the solid material and allowed to stand until it crystallized; this usually took some months, and even then the hil only partially solidified; but all our experiments to bring about a more rapid or complete crystallization gave unsatisfactory results. The solid was freed from adhering oil with filter paper and recrystallized from alcohol until it showed the constant melting point 107°, when it was dried *in vacuo*.

I. 0.1502 gram substance gave 0.1190 gram AgBr + AgI.

II. 0.1807 gram substance gave 0.1446 gram AgBr + AgI.

III. 0.1981 gram substance gave 10.30 cc. N_2 at 22° and 755 mm.

	Calculated for $C_6HIBr(NO_2)_2CH(CO_2C_2H_5)_2$	Found I	Found II	Found III
Br + I	38.98	38.79	39.18	....
N	5.27	...	...	5.85

The structure of this substance follows from that assigned

to the diioddinitrobenzene, as it can be prepared by the action of sodic malonic ester on this compound.

Properties of 1-Iod-2-brom-4,6-dinitrophenyl-3-malonic Ester.—It forms short, thick, lemon-yellow crystals which melt at 107°. It is easily soluble in methyl alcohol, ether, acetone, amyl alcohol, chloroform, ethyl acetate, low-boiling ligroin, benzene or toluene; soluble in hot alcohol, slightly soluble in cold; nearly insoluble in high-boiling ligroin. Alcohol is the best solvent for it. Sodic hydroxide converts it into a blood-red soluble salt, and this change of color was of use during the preparations in determining which portions of the product contained this substance.

Still another product of the action of sodic malonic ester on triiodbromdinitrobenzene was isolated by fractional crystallization, but it occurred in such small quantity that it could not be purified, especially as its decomposition point was too indefinite to give a criterion of purity. It was yellow and began to turn dark at 230°, growing darker till 250°, where it melted. Specimens showing this behavior toward heat, and crystallized until crystals and evaporated mother liquors behaved alike, gave results on analysis differing by several per cent.

1,3,5-Triiod-2-brom-4,6-dinitrobenzene and Sodic Ethylate.—To a solution of ten grams of the substituted benzene in 100 cc. of dry benzene were added 100 cc. of a solution of sodic ethylate in absolute alcohol, which contained one molecule of the ethylate for each atom of halogen present. The mixture was allowed to stand in a tightly corked flask for 7 days, during which time a considerable quantity of solid had crystallized out on the sides of the flask. The liquid was then allowed to evaporate spontaneously and the resulting yellow crystals washed with water (which gave a test for halogen) and recrystallized from alcohol until they showed the constant melting point 148°, when the substance was dried at 100°.

I. 0.2330 gram substance gave 0.1317 gram CO_2 and 0.0116 gram H_2O.

II. 0.1228 gram substance gave 0.1751 gram AgBr + AgI.

III. 0.1284 gram substance gave 0.1844 gram AgBr + AgI.

IV. 0.3027 gram substance gave 6.6 cc. N_2 at 20° and 763.4 mm.

	Calculated for $C_6I_3BrNO_2OC_2H_5$	Found I	II	III	IV
C	15.38	15.41	...	...	....
H	0.80	0.56	...	...	....
I_3 + Br	74.00	...	73.55	74.11	....
N	2.24	...	...	....	2.56

The substance has been formed, therefore, by the replacement of a nitro group by an ethoxy group. Its constitution follows from that of the mother substance.

Properties of the 1,3,5-Triiod-2-brom-6-nitrophenetole, $C_6I_3Br(NO_2)OC_2H_5$.—It crystallizes in very light pink, flattened needles with sharp ends, which in quantity have the appearance and luster of asbestos. From methyl alcohol or ligroin the needles are deposited in groups shaped like a dumbbell. It melts at 148°, and is soluble in ether, acetone, chloroform, tetrachloride of carbon, ethyl acetate or toluene; nearly insoluble in cold alcohol, moderately soluble in hot; moderately soluble in methyl alcohol, benzene or ligroin; soluble in hot glacial acetic acid, very slightly soluble in cold. Ethyl alcohol is the best solvent for it.

The fact that the wash waters from the crude phenetole gave a test for a halogen would indicate that a second compound had been formed by the action of sodic ethylate on the triiodbromdinitrobenzene, but a careful search for it gave no indication of its presence.

1,3,5-Triiod-2-brom-6-nitroanisole, $C_6I_3Br(NO_2)OCH_3$. — Ten grams of the triiodbromdinitrobenzene dissolved in dry benzene were treated with enough sodic methylate dissolved in methyl alcohol to give one molecule of the methylate to each atom of the halogen, and the mixture was allowed to stand in a corked flask for three days, when it was found that a considerable amount of solid had separated on the sides of the flask, and the liquid had taken on a slight reddish tint. It gave a slight test for halogens. It was allowed to evaporate spontaneously and the residue, after a thorough washing with

water, was crystallized from alcohol until it showed the constant melting point 163°, when it was dried at 100°.

I. 0.1499 gram substance gave 0.2206 gram AgBr + AgI.
II. 0.2102 gram substance gave 0.3092 gram AgBr + AgI.

	Calculated for $C_6I_3BrNO_2OCH_3$	Found I	Found II
Br + I	75.57	75.97	75.95

Properties of 1,3,5-Triiod-2-brom-6-nitroanisole. — It forms slightly yellowish needles, which melt at 163°. It is easily soluble in ether, acetone, chloroform, ethyl acetate, benzene or toluene; tolerably soluble in methyl alcohol; nearly insoluble in cold ethyl alcohol, more soluble when hot. A mixture of equal parts of benzene and alcohol is the best solvent for it.

Five grams of triiodbromdinitrobenzene were dissolved in benzene and treated with enough sodic phenylate to remove all the halogen from it. The sodic phenylate was made by treating the calculated amount of sodium with a little water and adding the sodic hydroxide thus formed to phenol in excess. After adding the sodium phenylate enough alcohol was added to the mixture to just dissolve it, and the whole was allowed to stand in a corked flask for a week, after which tests for a halogen or nitrite gave negative results. It was next heated on the steam bath for one hour and a half, and again tested for halogen or nitrite with negative results. The solvents were then allowed to evaporate spontaneously and the residue was washed with water till free from phenol and inorganic matter, when one crystallization from benzene and alcohol raised its melting point to 280°. There can be little doubt, therefore, that it was the unchanged triiod compound, which melts at 292°.

Reduction Experiments

Triiodbromnitrophenetole with Zinc and Acetic Acid.—Two grams of the phenetole mixed with a few cc. of alcohol were treated with zinc and 80 per cent. acetic acid and the action allowed to go on at ordinary temperatures. In a few hours the substance had dissolved completely, when the zinc was

filtered out and water added to the filtrate, which threw down a precipitate. Extraction with ether removed most of the product, but to be certain that no considerable amount was lost the zinc was precipitated with sodic hydroxide not in excess, and the zincic hydroxide extracted with alcohol, while the filtrate from it was extracted with benzene, but very little additional solid material was obtained by these two last extractions. The main product left by the evaporation of the ether was a white solid which rapidly turned dark on exposure to the air and melted (crude) at about 60°. As the purification of this free amino compound would evidently require a large amount of material, we converted it into the hydrochloride by saturating its solution in dry benzene with dry hydrochloric acid gas. The precipitate formed in this way was filtered out and dried between filter papers, as we feared heat might decompose it.

0.1765 gram substance gave 0.1688 gram AgCl.

	Calculated for $C_6H_4OHNH_2HCl$	Found
Cl	24.40	23.68

The action of the zinc and acetic acid on the phenetole, therefore, consisted, in addition to the reduction of the nitro group, in the replacement of all the halogen atoms by hydrogen and the saponification of the phenetole to the phenol. The new substance must be the *m*-aminophenol, the hydrochloride of which melts, according to Ikuta,[1] at 229°. Our crude product melted at 210°, which was raised by one crystallization from dilute hydrochloric acid to 225°, supporting the conclusion derived from the analysis.

1,3,5-Triiod-2-brom-4,6-dinitrobenzene with Zinc and Acetic Acid.—Five grams of the triiod compound mixed with 80 per cent. acetic acid and alcohol in equal volumes were allowed to stand with zinc at ordinary temperatures for several hours, but as there seemed to have been very little action, the mixture was heated on the steam bath, when the solid gradually dissolved. After it had disappeared entirely, the dark-colored solution was diluted with water, filtered from the excess of

[1] THIS JOURNAL, **15**, 40.

zinc and extracted with ether. The residue, after the spontaneous evaporation of the ether, was extracted with gasolene, which yielded, on evaporation, spindle-shaped crystals and rosettes, and these were crystallized from a mixture of benzene and ligroin, giving spindles, and finally from alcohol until they showed the constant melting point 92°. The crystals from alcohol were prisms. This melting point, the crystalline form, and the solubilities of the compound, suggest the 5-brom-*m*-phenylenediamine,[1] which melts at 93°–94°; and as this would be the most probable product of the reaction, there can be no doubt about the nature of the substance.

The same 5-brom-*m*-phenylenediamine was obtained by the action of iron and 80 per cent. acetic acid, the mixture being heated on the steam bath for two days, after which the iron was precipitated with sodic carbonate and sodic hydroxide, and both the precipitate and filtrate extracted with ether. The extract crystallized from alcohol showed the melting point 92°. Tin and hydrochloric acid seemed to give the same product, but the experiment was tried on too small a scale to give decisive results.

Stannous chloride, on the other hand, seemed to act very slightly on the triiodbromdinitrobenzene under the conditions used by us, as, after heating a mixture of one gram of it with alcohol, water (equal volumes) and a freshly prepared solution of stannous chloride for 8 hours on the steam bath, crystals separated on cooling which weighed 0.57 gram and melted after one crystallization from benzene and alcohol at 278°, while an additional precipitate obtained by adding water to the alcoholic filtrate melted after one crystallization at 260°. We inferred, perhaps somewhat rashly, that these consisted of the unaltered substance (melting at 292°), and did not repeat the experiment.

Sulphurous dioxide dissolved in 50 cc. of alcohol and 10 cc. of water had no perceptible action on the triiodbromdinitrobenzene, and the liquid gave no test for halogen after the experiment.

[1] Jackson and Gallivan: THIS JOURNAL, **18**, 242. Jackson and Calvert: *Ibid.* 486 (1896).

In the hope of finding a milder reducing agent which would not remove the iodine, we tried "iron by hydrogen" and sulphuretted hydrogen recommended by Merz and Weith.[1] For this purpose 2 grams of the triiod compound, with equal parts of alcohol and benzene, were mixed with the iron, and a stream of sulphuretted hydrogen passed through the mixture for 10 hours. The solution was then filtered from the ferrous sulphide and warmed gently to remove the excess of sulphuretted hydrogen, after which it was extracted with ether and the extract crystallized first from benzene and ligroin, when it showed the characteristic spindle forms, and then from alcohol, which raised its melting point to 92°, so that it is the 5-brom-*m*-phenylenediamine.

The experiments just described showed with tolerable certainty that acid reducing agents removed the iodine from the triiodbromdinitrobenzene if they acted at all, and we next tried an alkaline agent in the hope of confining the reduction to the nitro groups. As the usual alkaline reducer, sulphuretted hydrogen with ammonic sulphide, was inadmissible because of the danger of the replacement of halogens by other groups, we used ferrous hydroxide. Ten grams of triiodbromdinitrobenzene dissolved in alcohol were mixed with five times the amount of ferrous hydroxide needed for complete reduction. The ferrous hydroxide was made by dissolving the calculated weight of iron in hydrochloric acid, taking care to avoid a large excess of the acid, and treating this ferrous chloride with sodic hydroxide in a flask closed with a cork carrying a Bunsen valve, until a very slight alkaline reaction was obtained. If this remained after shaking, enough ferrous chloride was added to destroy the sodic hydroxide, as it had been found that even a very small excess of this substance reduced the yield to a considerable extent. After adding the triiod compound to the ferrous hydroxide in the flask its color changed quickly from light green to black. The mixture was allowed to stand for two days with frequent shaking and warming on the steam bath, and then the solution was filtered off. The filtrate, as was expected, yielded

[1] Z. Chem., **1869**, 242.

very little solid on extraction with ether and with benzene, but the main product was obtained from the ferroferric hydroxide by drying and extracting it with alcohol and also with benzene. The combined extracts furnished a solid which, after crystallization from a mixture of benzene and alcohol, showed the constant melting point 187°, when it was dried on a porous plate in a desiccator.

0.1302 gram substance gave 0.2059 gram AgBr + AgI.

	Calculated for $C_6I_3Br(NH_2)_2$	Found
I_3 + Br	81.59	81.67

The reduction therefore has been confined to the nitro groups.

Properties of 1,3,5-Triiod-2-brom-4,6-diaminobenzene.—It crystallizes in short, rather thick, grayish white needles which melt at 187°. It is soluble in ether, chloroform, benzene or toluene; easily soluble in hot alcohol, very slightly in cold. A mixture of benzene and alcohol is the best solvent for it. The yield was very small, principally due, it seemed, to the tenacity with which the ferroferric hydroxide retained the organic substance; we had enough of it, however, to make the hydrochloride.

Hydrochloride of Triiodbromdiaminobenzene, $C_6I_3BrNH_2NH_3Cl$.—A small amount of the diamine was dissolved in benzene (dried over sodium) and the solution saturated with dry hydrochloric acid gas. The precipitate formed was filtered out, washed with dry benzene and dried on a porous plate in a desiccator.

0.0643 gram substance heated to constant weight at 100° lost 0.0039 gram.

	Calculated for $C_6I_3BrNH_2NH_3Cl$	Found
HCl	6.02	6.06

The analysis made with such a small quantity can be regarded only as indicating the probable composition of the substance, but it shows with certainty that the number of halogen atoms in the diamine has reduced its basic properties

in a very marked degree, as the hydrochloride is decomposed at 100°

Triioddinitrobenzene with Zinc and Acetic Acid.—The remainder of this paper contains an account of parallel experiments with other triiod compounds.

Two grams of 1,3,5-triiod-4,6-dinitrobenzene[1] mixed with 80 per cent. acetic acid, to which an equal volume of alcohol had been added, were allowed to react with zinc at ordinary temperatures for several hours, when, upon extracting the filtered and diluted solution with ether, a light colored solid was obtained, which blackened so rapidly that there was no chance of purifying it without work on a large scale. To avoid this we determined the amount of iodine removed by the reducing agent by precipitating it as argentic iodide, and found in one experiment 47 per cent., in another 81 per cent., of the iodine had been removed. No pains had been taken to carry on these two reductions under the same conditions, or to bring them to an end, so that the want of agreement was not surprising; and no further work was done in this line, as our object had been accomplished, which was to show that zinc and acetic acid remove iodine from the triioddinitrobenzene.

1,3,5-Triiodaniline and Reducing Agents.—On heating a small amount of triiodaniline melting at 187° with tin and hydrochloric acid on the steam bath for several hours no evidence of a reaction could be found, as a test for iodine with chlorine water and carbonic disulphide gave a negative result, and the undissolved solid melted at 186°, showing it was unaltered triiodaniline.

Half a gram of the triiodaniline heated with 80 per cent. acetic acid and zinc on the steam bath for several hours gave a solution which on cooling deposited crystals, and these, after purification with benzene and alcohol, melted at 185°, showing they were unaltered triiodaniline. There was obtained, however, a slight test for iodine in the liquid, so that there was probably some action, but only a little, as most of the triiodaniline was recovered. We do not feel that these

[1] Jackson and Langmaid: THIS JOURNAL, **32**, 304 (1904).

experiments settle the matter, however, as it is possible other conditions might bring about a removal of most of the iodine.

1,3,5-Triiod-2-brombenzene with Zinc and Acetic Acid.—Five grams of triiodbrombenzene mixed with 80 per cent. acetic acid and 25 cc. of alcohol were heated with zinc on the steam bath until the solid had disappeared completely. The solution was then filtered from the zinc and largely diluted, when a precipitate fell which was extracted with ether, and the extract crystallized from alcohol until it showed the constant melting point 92°, which is that of the *p*-iodbrombenzene,[1] C_6H_4IBr; the action therefore had consisted in replacing the two atoms of iodine ortho to the bromine by hydrogen. But, although this was the principal product in this case, it was not the only one, as shown by the following determination of the amount of halogen removed in a similar reduction.

1.0525 grams of substance reduced with zinc and acetic acid yielded 1.2180 grams of argentic halide.

Calculating this as argentic iodide we obtain

	Calculated	Found
2I	47.47	62.57
3I	71.04	...

It is obvious that the precipitate may have contained argentic bromide also, but in any case the amount of argentic halide obtained shows that a secondary reaction had taken place, accompanied by a further removal of halogen.

1,3,5-Triiodbenzene and Sodic Ethylate.—Triiodbenzene[2] was dissolved in dry benzene and enough sodic ethylate in absolute alcohol added to give one molecule for each atom of iodine. After boiling for three hours no test for iodine was obtained, nor was the result better after boiling for 5 more hours. Upon cooling crystals separated which, after purification, showed the melting point 181°, and were therefore unchanged triiodbenzene, which melts at this temperature. The mother liquor from these crystals was evaporated to a small volume and heated for two more hours with a strong solution of sodic ethylate, but no test for iodine could be obtained.

[1] Griess: Jahresb. d. Chem., **1866**, 452. Körner: Gazz. chim. ital., **4**, 339.
[2] This Journal, **29**, 300 (1904).

1,3,5-Triiod-2-brombenzene with Sodic Ethylate.—Ten grams of the triiodbrombenzene were dissolved in dry benzene and mixed with 250 cc. of absolute alcohol containing enough sodic ethylate to give one molecule for each atom of halogen. No change was visible in the cold, and no test for a halogen could be obtained, but after boiling on the steam bath for 3 hours there was a slight test and after 12 additional hours of boiling the test for halogen was distinct. On evaporating to dryness a somewhat tarry residue was left, from which we succeeded in isolating only unaltered triiodbrombenzene, recognized by its melting point, 146°, and two determinations of halogens. It seems therefore that sodic ethylate acts upon the triiodbrombenzene but only to a very limited extent.

The research will be continued.

THE CONDUCTIVITY OF CERTAIN SALTS IN METHYL AND ETHYL ALCOHOLS AT HIGH DILUTIONS

By H. R. Kreider and Harry C. Jones

This work is a continuation of that already discussed in a previous article.[1] In our earlier work we measured the conductivity of certain salts in very dilute solutions of ethyl alcohol and methyl alcohol. The salts employed were potassium iodide, ammonium bromide, potassium sulphocyanate, lithium nitrate, sodium iodide, calcium nitrate, cobalt chloride and copper chloride. The conductivities of these salts were measured in solutions ranging in concentration from N/1600 to N/51200. The conductivities of these salts in more concentrated solutions had been previously measured by Jones and his coworkers.

In our former work a well defined maximum in conductivity with increasing dilution was noted in solutions of a number of salts. Certain relations between these maxima were pointed out. The ratio between $\mu\infty$ for a certain salt in methyl alcohol, and $\mu\infty$ for the same salt in ethyl alcohol

[1] This Journal, **48**, 282 (1911).

was found to be a constant for different binary salts. The following values were obtained for $c = \mu_\infty$ methyl alcohol/μ_∞ ethyl alcohol.

Binary Electrolytes

	c
$LiNO_3$ at 0°	2·37
NaI at 0°	2·37
NH_4Br at 25°	2·44
NaI at 25°	2·17

Ternary Electrolytes

$CoCl_2$ at 0°	3·68

The conductivities of other salts at the same high dilutions have now been measured, with the object of seeing whether the relations given above are general. The salts used were sodium bromide, lithium bromide and cobalt bromide. The work with potassium sulphocyanate in methyl alcohol was repeated, and more satisfactory results obtained.

Most of the measurements were made at the dilution of complete dissociation. The values of μ_∞ for the same salt in methyl and ethyl alcohols are then compared with each other, and also with the value of μ_∞ for the same salt in water. The apparatus employed is the same as that previously described, with some minor improvements. The same cells, with concentric platinum cylinders as electrodes, were used. One cell having the electrodes closer together and a smaller constant was also employed.

Both salts and solvents were purified with special care. A solution of a certain concentration was then prepared as the mother solution, and from it the other solutions were made. Some of the solutions were as dilute as N/102400.

The precautions observed were the same as those previously discussed. In addition, greater care was exercised in purifying the methyl alcohol. It is very difficult to get methyl alcohol in large quantities in such a state of purity that its specific conductivity is low enough to obtain good results for such dilute solutions. It was found that the conductivity of methyl alcohol could be much reduced by treating the

alcohol with a little dilute sulphuric acid. The best results were obtained when the alcohol was in contact with the acid not more than twelve hours. The alcohol was then distilled from the acid and boiled with, and distilled from lime at least twice.

The results obtained are given in the following tables:

Table I.—Conductivity of Sodium Bromide in Methyl Alcohol

V	μ_v 0°	μ_v 25°
800	53.0	77.4
1600	58.2	83.9
3200	62.3	88.6
6400	63.8	91.3
12800	64.1	92.8
25600	64.6	93.3
51200	69.1	101.0

Table II.—Conductivity of Sodium Bromide in Ethyl Alcohol

V	μ_v 0°	μ_v 25°
800	19.9	33.6
1600	23.1	36.5
3200	24.0	38.3
6400	24.6	39.6
12800	24.9	40.2
25600	24.6	40.2
51200	24.9	37.6
102400	21.0	32.9

Table III.—Conductivity of Lithium Bromide in Methyl Alcohol

V	μ_v 0°	μ_v 25°
800	40.9	57.2
1600	44.5	64.8
3200	45.6	68.7
6400	48.2	69.8
12800	47.8	73.7
25600	49.5	74.6

Table IV.—Conductivity of Lithium Bromide in Ethyl Alcohol

V	μ_v 0°	μ_v 25°
1600	17.2	27.8
3200	18.3	28.9
6400	18.3	29.3
12800	18.4	28.9
25600	18.3	29.4
51200	18.3	30.1
102400	18.1	27.8

Table V.—Conductivity of Potassium Sulphocyanate in Methyl Alcohol

V	μ_v 0°	μ_v 25°
1600	70.7	99.9
3200	75.8	106.2
6400	72.9	102.9
12800	73.9	104.5
25600	72.1	105.4
51200	86.1	132.2

Table VI.—Conductivity of Cobalt Bromide in Methyl Alcohol

V	μ_v 0°	μ_v 25°
800	19.0	23.6
1600	21.6	27.5
3200	24.9	32.4
6400	29.1	37.0
12800	33.1	44.2
25600	36.8	50.6
51200	38.6	65.9

Table VII.—Conductivity of Cobalt Bromide in Ethyl Alcohol

V	μ_v 0°	μ_v 25°
800	57.9	77.3
1600	61.3	82.0
3200	62.2	87.4
6400	64.7	95.1
12800	66.9	106.7
25600	70.1	106.6
51200	96.2	124.0

Table VIII.—Ratios of Conductivities and Fluidities

$\frac{\text{Flu. W}}{\text{Flu. E}}$		$\frac{\mu\infty\ \text{W}}{\mu\infty\ \text{E}}$		$\frac{\text{Flu. M}}{\text{Flu. W}}$		$\frac{\mu\infty\ \text{M}}{\mu\infty\ \text{W}}$		$\frac{\text{Flu. M}}{\text{Flu. E}}$		$\frac{\mu\infty\ \text{M}}{\mu\infty\ \text{E}}$	
	0°				0°				0°		
		$LiNO_3$	2.26			KI	1.01			NaBr	2.32
		NaI	2.31			NaI	1.02			$LiNO_3$	2.37
		KI	2.33			$LiNO_3$	1.05			NaI	2.37
		NaBr	2.44			NaBr	1.05			KCNS	2.53
										LiBr	2.60
			2.33				1.03				
0.995		$CoCl_2$	3.70	2.18		$CoCl_2$	0.99	2.17			2.44
										$CoCl_2$	3.67
	25°				25°				25°		
										NaI	2.17
										KCNS	2.27
										LiBr	2.38
										NH_4Br	2.44
										NaBr	2.59
0.817				1.65				2.27			2.37

Discussion of Results

Table I gives the conductivities of sodium bromide in methyl alcohol at both 0° and 25°. At 0° we have complete dissociation probably at 6400 liters. At 25° complete dissociation is not attained until a dilution of 12800 liters is reached.

Table II gives the conductivities of sodium bromide in ethyl alcohol at 0° and 25°. Complete dissociation is reached at both temperatures at a dilution of 12800 liters. At the volume 102400 there is a marked decrease in conductivity, probably due to the great solvation at this extremely high dilution. The same fact may be noticed in several other tables where ethyl alcohol is used as a solvent.

Table III gives the conductivity of lithium bromide in methyl alcohol. At 0° complete dissociation probably is reached at 6400 liters. At 25° there is no maximum in conductivity, but the rate of increase is much smaller above 3200 liters than it is at greater concentrations, indicating that the maximum is nearly reached.

Table IV gives the conductivity of lithium bromide in ethyl alcohol. At 0° there is complete dissociation at 3200 liters. At 25° it is complete at 6400 liters. For both temperatures at higher dilutions the conductivity remains almost constant up to a dilution of 102400 liters, where, at 25° there is a marked decrease in the conductivity.

Table V gives the conductivity of potassium sulphocyanate in methyl alcohol. This is a repetition of work previously done. We have now obtained more concordant results. Here complete dissociation is reached at both temperatures at 3200 liters.

Tables VI and VII give the conductivity of cobalt bromide in both methyl alcohol and ethyl alcohol. Here there is no maximum in conductivity. This is probably due to the fact that cobalt bromide is much solvated.

Table VIII gives, in the right-hand columns, the ratios of the values of μ_∞ for a number of salts in the following solvents: Water and ethyl alcohol; methyl alcohol and water; and methyl alcohol and ethyl alcohol. When we consider the large magnitude of the experimental error in working at these

great dilutions it is quite probable that the relation, μ_∞ for one solvent/μ_∞ for another solvent $= c$, holds where the salts have approximately the same degree of solvation.

That there is a constant relation between the values of μ_∞ for different salts in different solvents we would expect. When a certain salt in two different solvents is completely dissociated, we have either the same number of ions present, or, relative to the concentration, the same number of ions present.

When the point of complete dissociation is reached at the same dilution in both solvents, we have the same number of ions present in the same volume of the two solvents. When such a point of complete dissociation exists at different dilutions in solutions of the two solvents, the number of ions in equal volumes of the two solutions varies directly as the concentration, and we have, relative to the concentration, the same number of ions present.

Conductivity is a function of the number of ions present and the velocity with which these ions move. Since at the complete dissociation of a salt in solutions of two different solvents the number of ions is actually the same, or relative to the concentration the same, we can eliminate this factor—the number of ions—and consider only the velocities with which these ions move.

Two factors primarily determine ionic velocity. The ionic mass and volume, and the fluidity of the solution, which is, of course, the reciprocal of the viscosity. Assuming that the ionic masses and volumes of a certain salt in two different solvents at complete dissociation remain the same, then the velocities of the ions ought to vary as the fluidities of the respective solvents. Since the number of ions in the two solvents at the same dilution of the solutions is the same, the ionic masses and volumes being the same, the conductivities ought to vary directly as the fluidities of the solvents; the ratio between the values of μ_∞ in the various solvents ought to be the same as the ratio of the fluidities of these solvents. This, however, is not the case. If the ratios between the values of μ_∞ for the salts in the two solvents are not the same

as the ratios between the values for the fluidities of these solvents, the mass and probably the volumes of the solvated ions must differ in the two different solutions.

The fluidity of methyl alcohol at 0° is 123.9 while that of ethyl alcohol is 56.24. Since the fluidity of methyl alcohol is much greater than that of ethyl alcohol, we would expect the ions of a dissolved salt to move much faster in methyl alcohol, and, consequently, the conductivity of a solution of a salt at any concentration would be much greater in methyl than in ethyl alcohol. At complete dissociation, where the number of ions is the same in both solvents, we would expect the conductivity in methyl alcohol to be as much greater than that in ethyl alcohol as the fluidity of the former is greater than that of the latter. We would expect a direct relation between fluidity and conductivity.

Jones and his coworkers have shown that there is solvation in solutions in water, methyl alcohol, ethyl alcohol and solvents in general; and that this solvation increases with dilution. From this we know that at complete dissociation solvation is greater than at any dilution short of complete dissociation.

Since a molecule of methyl alcohol is much heavier than one of water the ion, for equal solvation, would be loaded down more in the former solvent, and the conductivity in methyl alcohol would be less than in water, even if the fluidities were the same. Again, the molecule of ethyl alcohol is heavier than the molecule of methyl alcohol. The equally solvated ion would, therefore, be heavier in ethyl alcohol and the conductivity less.

Table VIII[1] gives the ratios of the fluidities of three solvents—water, methyl alcohol and ethyl alcohol; also the ratio of μ_∞ for certain salts in these solvents at both 0° and 25°. Water and ethyl alcohol are first compared. Their fluidities are nearly the same, hence their ratio is nearly unity. The ratios between the values of μ_∞ for four salts in these two solvents are given. The mean of these values is 2.33 with a

[1] The values for μ_∞ of the various salts in water as a solvent given in Table VIII are taken from the work of Jones and Getman (Z. physik. Chem., **49**, 385 (1904)).

minimum of 2.26 and a maximum of 2.44. This mean ratio of the values is much greater than the ratio of the fluidity values of the two solvents, indicating that the ion in ethyl alcohol moves much more slowly, compared with its velocity in water, than we would expect from a comparison of the fluidities of the solvents. The only explanation of this fact seems to be that the ion is loaded down much more in ethyl alcohol than in water, and, hence, its velocity diminished, giving a much lower conductivity. The only way in which it could be loaded down is by one or more molecules of the solvent being united with the ion.

In the second column of Table VIII water and methyl alcohol are compared. The fluidity of methyl alcohol is much greater than that of water. It is 2.18 times as great at 0°. There are four μ_∞ ratios. The mean is 1.03. The maximum is 1.05 and the minimum is 1.01. The fact that the fluidity of methyl alcohol is much greater than that of water, while the conductivity of salts in methyl alcohol is but little greater, indicates that in methyl alcohol the ion is loaded down more than in water, and its velocity more retarded. This, of course, we would expect from the masses of the molecules alone, since those of methyl alcohol are so much greater than those of water.

In the third column, methyl alcohol and ethyl alcohol are compared. The fluidity of methyl alcohol is 2.17 times as great as that of ethyl alcohol at 0°; while the mean of the conductivity ratios is 2.44. This would indicate that in ethyl alcohol the ions are loaded down more than in methyl alcohol, which, again, we would expect. This is the case at both 0° and 25°. The difference is, however, much less at 25° than at 0°. At 25° the ratios of fluidity and conductivities are more nearly equal. This would indicate that at the higher temperatures the ions are less retarded and, accordingly, less solvated, as Jones and Bassett[1] have pointed out.

The fact that the equation

$$\mu_\infty s / \mu_\infty s' = c,$$

where s and s' are any two of the solvents above mentioned,

[1] THIS JOURNAL, **34**, 290 (1905).

holds for the values in Table VIII is in itself important. But it further shows approximately which salts are solvated to the same extent in any given solvent, since it holds only in such cases. For such salts as are not solvated to the same extent in a given solvent the equation will, of course, not hold.

We have worked with one salt, cobalt chloride, which is very hydroscopic, and which has been shown by Jones and his coworkers to be strongly hydrated in aqueous solutions. This salt shows a greater departure in the ratios of its conductivities from the ratios of fluidities than is shown by the other salts which we studied. From the results in the column μ_∞ W/μ_∞ E we see that cobalt chloride is much more loaded down in ethyl alcohol than it is in water. The value of the ratio of μ_∞ in the two solvents, 3.70, is greater than that of the other salts, 2.33, and much greater than the value of the fluidity ratio of the two solvents, which is 0.995.

From the column μ_∞ M/μ_∞ W we see that the ions of cobalt chloride are loaded down more in methyl alcohol than in water, and that the ratios of the conductivities deviate more from the ratios of fluidities than in the case of the other salts; but this deviation ought not to be as great as in the case of water and ethyl alcohol, since there is not so much difference between the masses of the molecules of methyl alcohol and water as there is between those of ethyl alcohol and water. Comparing the figures in this column we find that this is the case, since 0.99, the value of the ratio of the conductivities of cobalt chloride, is less than 1.03, the ratio for the other salts, and very much less than 2.18, the ratio of the fluidities of the two solvents.

We would expect the cobalt chloride ions to be loaded down to the greatest extent in ethyl alcohol, and that the conductivity in ethyl alcohol would be lower than in methyl alcohol. This difference should be greater than that of the other salts which are less solvated. We would expect the ratio μ_∞ M/μ_∞ E for this salt to show a greater departure from the ratio of the fluidities of the two solvents than is shown by the other salts. A comparison of the figures in column μ_∞ M/μ_∞ E shows this to be the case.

Although this does not give us a method for measuring the actual degree of solvation in the different solvents, it throws some light on the relative masses of the solvents combined with any given ion in these dilute solutions.

It has been shown that water hydrates salts in more concentrated solutions, and that this hydration increases with the dilution, as we would expect from the mass action of the solvent. If in water these salts are solvated, it is evident from the above facts that in methyl alcohol there is a larger mass of the solvent in combination with the ion. This does not necessarily indicate that in the latter case there are more molecules of the solvent in combination with the ion. There may be the same number, or even less, in combination, but the molecules of methyl alcohol being so much heavier might cause the difference in conductivity. In ethyl alcohol also there is a larger molecular mass than in water or in methyl alcohol, but here, again, the difference between the ratios may be due to the heavier molecules of ethyl alcohol.

It is evident that this factor of solvation at complete dissociation plays a role in our present method for calculating dissociation by means of the conductivity of the solution. Here we employ the equation $\alpha = \mu_v / \mu_\infty$. In the above discussion μ_∞ is shown not to be a true function of the actual number of ions present, but is smaller than it ought to be in consideration alone of the number of ions present. Furthermore, it has been shown that there is solvation in more concentrated solutions also; hence, μ_v is not a function only of the number of ions present in the solution in question. The deviations of the values of μ_v and μ_∞ from the true values are probably of the same order of magnitude, if not very nearly equal, so that the validity of the equation in calculating conductivity is probably not seriously affected.

SUMMARY

We have measured the conductivities of very dilute solutions of a number of salts in methyl alcohol and ethyl alcohol.

In most cases the values of μ_∞ were found. These values bear a definite relation to one another.

It was found that the ratio of the value of μ_∞ for a certain salt in one solvent and the value of μ_∞ for the same salt in another solvent is nearly constant for salts which are solvated to approximately the same extent.

In cases where one salt is solvated very much more than another the value of μ_∞ is generally less for the more solvated salt.

We have compared the ratios of μ_∞ for certain salts in two different solvents with the ratios of the fluidities of these solvents. In all cases the former ratios show a departure from the latter, the value of μ_∞ in the solvent which has the greater molecular mass always being less than we would expect from the ratio of the fluidities alone of the two solvents. Those salts which are known to be solvated to the greatest extent show the greatest difference between these ratios.

JOHNS HOPKINS UNIV.
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A STUDY OF THE HYDROGEN ELECTRODE, OF THE CALOMEL ELECTRODE AND OF CONTACT POTENTIAL

BY N. E. LOOMIS AND S. F. ACREE

(We are indebted to the Carnegie Institution of Washington for aid in this work.)

I. INTRODUCTION

For several years we organic chemists have felt the need of some direct, very rapid, and accurate method for determining the hydrogen (also hydroxyl) ion concentration of dilute solutions. Such a method would be of special value in the study of many organic reactions involving, for example, the hydrolysis of salts or the saponification of esters, the reactions of addition products in cases of catalysis by hydrogen ions, and many others in which the system is gradually changing.

The methods commonly in use heretofore have presented serious difficulties in their general application. The conductivity method, for example, which has had the widest range

of application, rapidly diminishes in accuracy with increase in dilution of the solution, and furthermore, the measurement of small concentrations of acids in the presence of other electrolytes, especially the salts of these acids with weak bases, is almost impossible. Special methods, such as the use of diazoacetic ester, as suggested by Bredig and Fraenkel,[1] have been used brilliantly in some cases, but are too limited in their range of application. Methods involving titration are of course useless in systems in which a state of equilibrium is established comparatively quickly, for the equilibrium is disturbed as soon as any one of the components is removed.

Although colorimetric methods in the hands of Veley, Salm, Tizard, Szyszkowski and others yield beautiful results in many cases, it has been found that neutral salts affect the colors so greatly in other cases that the method is useless or at least uncertain.

The hydrogen electrode has been recognized by one of us as a possible instrument for the solution of this problem.[2] Particularly suggestive is the work of H. G. Denham,[3] who measured the degree of hydrolysis of several inorganic salts and of aniline hydrochloride. He obtained results agreeing extremely well with those determined by Bredig by the conductivity method. Efforts to duplicate his results and other work on similar lines in this laboratory at first met with serious difficulties, but these are being gradually overcome.

In view of the extreme importance of any favorable results in this field, it seemed worth while to make a careful study of the hydrogen electrode, with special reference to its constancy, the value of its potential in different acids, the ease of reproduction, etc.; in other words, to attempt to make it a standard electrode for use in the same way that calomel and mercurous sulphate electrodes are used. To make the hydrogen electrode an accurate instrument for measuring

[1] Z. Elektrochem., **11**, 525 (1905); Z. physik. Chem., **60**, 202 (1907).

[2] Desha: Diss., Johns Hopkins Univ., 1909. This work was begun in 1907–8, and reported at the Christmas meeting of the American Association for the Advancement of Science, in 1908. See Science, **30**, 624. Lapworth has also for some time advocated an attempt in this direction.

[3] J. Chem. Soc., **93**, 41 (1908).

hydrogen ion concentrations, the measurements must be made with a much higher degree of accuracy than has ordinarily been done.

Early in the investigation it was realized that much of the accuracy of the work would be dependent upon the constancy and ease of reproduction of the calomel electrodes which were used with the hydrogen electrode. For this reason the study of the calomel electrode was gone into very thoroughly.

The method of approaching the problem under consideration resolved itself into five lines of investigation:

1. The study of the relative efficiency of the apparatus used by others and of newer forms devised by us to eliminate various sources of error. The literature and our own experience in this laboratory have shown that there is still much to be done in this line. In this connection we cannot refrain from expressing our deep obligation to Professor H. N. Morse for his kindness in giving us many valuable suggestions when we needed the benefit of the rare knowledge and mechanical skill that have enabled him to overcome such great difficulties in his own researches.

2. The study of the calomel electrodes. A large number of calomel electrodes were prepared and measured against each other so that the value adopted for the potential of the calomel electrode was the average of a number and not dependent upon a single electrode.

3. The preparation of a large number of platinum electrodes which were intercompared by the method used for the calomel electrodes.

4. The direct comparison of the hydrogen electrode with the calomel electrode, involving experiments to determine the efficiency of various solutions in eliminating contact potential.

5. The application of the hydrogen electrode to the determination of the hydrogen ion concentration of various solutions. The hydrolysis of aniline hydrochloride and the effect of neutral salts upon the dissociation of acetic acid were especially studied (see the next article).

II. PREVIOUS WORK

The normal calomel electrode, composed of mercury, calomel and normal potassium chloride solution, was first used and described by Ostwald.[1] It is described as reproducible to within one millivolt. He gives the potential of the electrode as $+0.5600 + 0.0006(t°-18°)$. This value was determined by Rothmund[2] by the drop-electrode method.

A year later Coggeshall[3] made an extended study of calomel and mercurous sulphate electrodes as to constancy, ease of reproduction, best form of cell, effect of mechanical disturbance, etc. Although this work constituted the most complete study of standard electrodes made up to that time, it left much to be desired. The measurements of potential were made with a Lippman electrometer, which is a far less accurate method than that in which a potentiometer and sensitive galvanometer are used. He did not use the decinormal calomel electrodes at all. Although finding the mercurous sulphate electrodes to be on the whole more suitable for use than the calomel electrodes, he concluded that "bei Anwendung wohl gereinigter Chemikalien und einer Vorkehrung gegen Erschütterungswirkungen, wie eine solche in der partiellen Sandfüllung gegeben ist, sind ohne Mühe Normal-Quecksilber-Kalomel-Electroden herstellbar, deren electromotorische Kraft von dem Normal Wert um nicht mehr als 0.0008 Volt abweicht, und dies mit ausserordentlicher Konstanz."

Smale[4] was the first to make an extended study of the hydrogen electrode and his work was principally in connection with the oxygen-hydrogen gas element. He concluded that the material (platinum, palladium, gold and carbon) in the electrode used played no part in the electromotive force of the cell, provided that it was not acted upon chemically. The surface and size of the electrodes, above a certain limit, had no effect.

Wilsmore[5] repeated Smale's work and made allowance for

[1] Ostwald-Luther: "Physiko-Chemische Messungen," 3rd Edition, p. 441.
[2] Z. physik. Chem., **15**, 15 (1894).
[3] *Ibid.*, **17**, 62 (1895).
[4] *Ibid.*, **14**, 577 (1894).
[5] *Ibid.*, **35**, 296 (1900).

the contact potential of the solutions. In regard to the part played by the electrode, he arrived at the same conclusions as Smale. As his zero of potential he adopted the potential of the hydrogen electrode toward a solution normal with respect to hydrogen ions. On this basis he found the value of the normal calomel electrodes to be 0.283 volt. He calculated the contact potential of a large number of pairs of solutions, using data obtained by others, and studied the electromotive force of the hydrogen-oxygen gas battery and the potential of a large number of metallic electrodes.

Richards[1] found that the temperature coefficients increased with dilution of the solution, and that the decinormal calomel electrode is more uniform in its behavior than the electrodes containing normal potassium chloride solution. He determined the temperature coefficient of the decinormal electrode to be 0.00079. In this work he noticed certain gradual changes in the potential of the calomel cells, especially of those containing the more concentrated salt solutions.

In a later article[2] Richards and Archibald showed that this gradual change is caused by the formation of a complex mercuric ion by the interaction of the alkali chloride and the calomel. This decomposition is very slightly affected by light or air but is hastened by elevating the temperature or by increasing the concentration of the solution of the alkali chloride. The decomposition is almost negligible in 0.1 N solutions. This work was corroborated by experiments carried on simultaneously by Gewecke.[3]

Sauer,[4] in an extended study of various electrodes, including the systems

Hg—HgCl—N KCl
Hg—HgCl—0.1 N KCl
Hg—HgCl—N HCl
Hg—HgCl—0.1 N HCl
Hg—Hg_2SO_4—N H_2SO_4
Hg—Hg_2SO_4—0.1 N H_2SO_4

concluded that the normal potassium chloride-calomel elec-

[1] Z. physik. Chem., **24**, 39 (1897).
[2] *Ibid.*, **40**, 385 (1902).
[3] *Ibid.*, **45**, 685 (1903).
[4] *Ibid.*, **47**, 146 (1904).

trodes can be made up with a slightly greater degree of uniformity than can the decinormal electrodes, which were found to be reproducible to within about 0.2 millivolt. Light was found to have no effect upon the potential of the calomel electrodes. By direct comparison of the normal and decinormal electrodes he found that if the former is assumed to have a value of 0.560 volt at 18°, the latter will have a value of 0.612.

Sauer's observation as to the greater uniformity of the normal electrodes has been corroborated by Lewis and Sargent,[1] who have also placed emphasis upon the purification of materials and uniform methods of preparation of the calomel-mercury paste.

Palmaer[2] determined by the drop-electrode method that the absolute potential of the decinormal electrode at 18° is -0.5732 ± 0.0003. At the same temperature the value of the normal electrode is -0.56. This gives a difference of 0.013 between the potentials of the normal and decinormal electrodes. By direct comparison Sauer found the difference at 18° to be 0.052. Since the procedure of Sauer is probably a far more accurate method for determining differences in potential than is the drop-electrode method, it has seemed best to adopt Wilsmore's standard as the zero of potential, viz., the potential of the hydrogen electrode toward a solution normal with respect to hydrogen ions. If we use Sauer's value for the difference between the potentials of the normal and decinormal electrodes, the value of the decinormal electrode, according to Wilsmore's standard, becomes $-0.283 - 0.052 = -0.335$ at 18°. At 25° the potential of the decinormal electrode becomes $-0.335 - 0.0008(25° - 18°) = -0.3406$.

Besides the work briefly reviewed above, there has appeared an immense amount of work involving the use of the hydrogen electrode, the calomel electrode or other standard electrodes. In this connection may be mentioned the work of Lorenz and Mohn[3] on the neutral point of the hydrogen elec-

[1] J. Am. Chem. Soc., **31**, 362 (1909).
[2] Z. physik. Chem., **59**, 129 (1907).
[3] *Ibid.*, **60**, 422 (1907).

trode; that of Lorenz and Böhi[1] on the electrolytic dissociation of water; that of Lewis and Rupert[2] on the chlorine electrode; that of Naumann[3] on the electromotive force of the hydrogen-cyanogen gas element; that of Schoch[4] on the oxygen electrode; and many others.

III. THEORETICAL DISCUSSION

The theory of the hydrogen electrode is generally familiar. It will only be recalled here that according to Nernst the potential of the electrode toward the solution in which it is immersed is dependent upon the pressure of the hydrogen gas and upon the osmotic pressure of the hydrogen ions in the solution.

In the comparison of a calomel electrode against a hydrogen electrode in a solution whose hydrogen ion concentration is H', we find that if π represents the observed electromotive force, π_1 the potential of the calomel electrode against a hydrogen electrode when immersed in a solution with unit concentration of hydrogen ions, and π_2 the contact potential between the solutions of the system, then the equation

$$\pi = \pi_1 - \frac{RT}{F} \log_e H' + \pi_2$$

holds when the hydrogen gas is under atmospheric pressure. From this equation, when $T = (25 + 273)°$ we find that

$$\log_{10} H' = -\frac{\pi - \pi_1 - \pi_2}{0.0591}$$

The value of π is obtained by actual measurement with the potentiometer, π_1 is calculated from some system in which π_2 and $\frac{RT}{F} \log_{10} H'$ are known and π has been previously measured, and π_2 is calculated. The best system for determining the value of π_1 is

$$H_2\text{—}Pt \mid 0.1\ N\ HCl \mid 0.1\ N\ KCl \mid HgCl\text{—}Hg$$

in which π can be measured, $\frac{RT}{F} \log_e H' = 0.0591 \times \log_{10}$

[1] Z. physik. Chem., **66**, 733 (1909).
[2] J. Am. Chem. Soc., **33**, 299 (1911).
[3] Z. Elektrochem., **16**, 191 (1910).
[4] J. Phys. Chem., **14**, 665, 719 (1910).

0.0922, and π_2 can be calculated by some such formula as that of Planck.

Because of the difficulty of calculating π_2 exactly in many cases, attempts have been made to eliminate this potential by interposing between the two solutions in question a saturated solution of some highly soluble salt, the two ions of which have nearly the same migration velocity, such as ammonium nitrate, potassium chloride,[1] and others. The use of ammonium nitrate for this purpose has been advocated by Abegg and Cumming,[2] who claim that it practically eliminates the contact potential. On this assumption it was used by Denham in his measurements of the hydrolysis of aniline hydrochloride and a number of inorganic salts. That it does not do away entirely with the contact potential was shown by Desha. Some measurements of our own in this connection will be spoken of later.

In order to show a change of 0.1 per cent. in the hydrogen ion concentration of a solution, the measurements must be accurate to within 0.000025 volt, and an accuracy of 0.00001 volt was striven for. The question of the effect of temperature also comes into consideration. Since 1° makes a difference of 0.0008 volt in the potential of the decinormal calomel electrode, the temperature had to be kept constant to within about 0°.01.

IV. EXPERIMENTAL

1. *Apparatus*

The electromotive force measurements were all made with a Leeds and Northrup potentiometer calibrated by the Bureau of Standards. All measurements were made by the zero method, that is, the potentiometer was adjusted until there was no deflection of the galvanometer. The galvanometer was a Leeds and Northrup special high-sensibility, short-period instrument of the Marvin type. It had a sensibility of 117, a period of 1.7 seconds, and a resistance of 215 ohms.

[1] After this article was in type we learned of the very important work of Bjerrum on the use of a saturated solution of potassium chloride to eliminate contact potential (Z. Elektrochem., **17**, 389; Z. physik. Chem., **53**, 428). His results agree very closely with ours.

[2] Z. Elektrochem., **13**, 17 (1907).

As primary standards of potential we used two Weston standard cells kindly loaned to us by the Bureau of Standards and calibrated by them from time to time.

The apparatus was tested for leakage currents and thermal effects by making various commutations and found to be free from them within the limit of accuracy of the work. With this apparatus measurements could be made to within 0.00001 volt with a high degree of accuracy. The apparatus was tested by measuring the electromotive force of one standard cell against the other.

Value obtained by Bureau of Standards = 1.01892.

Value measured on the potentiometer = 1.01892.

Value after correcting in accordance with calibration of potentiometer = 1.01892.

The experiments were all carried out at 25° C. The thermometer used in the bath was compared about once a week with a Beckmann thermometer, which was in turn compared to within 0°.002 with two mercury thermometers calibrated by the Bureau of Standards to about 0°.001.

For a constant-temperature bath there was used a glass aquarium 36 × 16 × 15 inches, partially filled with oil, as illustrated in Figs. 1, 7, 7*a*. At first an attempt was made to use an ordinary water bath, then an oil bath immersed in a water bath, but electric leakage currents in both cases made it necessary to adopt the oil bath. The oil used was a light lubricating oil, very transparent, nearly colorless and odorless, and free from sulphur, as was shown by the mercury test. The heating was accomplished by an electric light, (*L*) in Fig. 7, which was regulated by a relay and thermoregulator. A fan stirrer situated at one end of the aquarium drove the oil down and under a glass plate placed four inches above the bottom to the further end of the bath, where oil rose and returned through the thermoregulator and above the plate to the stirrer. The glass plate also served as a support for the apparatus used. Under the glass plate is a cooling coil not shown in the figures. The thermoregulator was a toluene grid of the type in use in this laboratory. The temperature regulation was constant to within 0°.01.

The hydrogen used for the hydrogen electrode was generated electrolytically from ten per cent. sodium hydroxide solution, as shown in (*I*), Fig. 7, nickel electrodes being used. A current of about one ampere was generally employed. To remove the last traces of oxygen from the hydrogen, it was passed through an electrically heated tube containing palladium asbestos. The tube (*M* in Fig. 7 and *A* in Fig. 7*a*) was made of Jena combustion tubing, 6 mm. in diameter, and was fitted with a mercury trap at one end. It was covered with a layer of asbestos and inserted in a close fitting brass tube (*N* in Fig. 7) having an inner diameter of 9 mm. Around the brass tube were wrapped 60 ohms of "No. 38 Nichrome" ribbon, the layers being insulated from each other by asbestos paper. When this coil, in series with 73 ohms (a 32 and a 16 c. p. lamp in parallel) was connected to the 110-volt city circuit a temperature of 170° C. was obtained. A slow flow of gas through the tube had no appreciable effect upon the temperature.

From the palladium asbestos tube the hydrogen passed through a washing apparatus (*B*, in Figs. 7 and 7*a*), which contained the same solution as that used around the hydrogen electrode.

The general arrangement of the bath, motor, hydrogen generator and potentiometer is shown in the accompanying photograph, Fig. 1. Since the metallic tank in which the aquarium is placed hides the lower part of the apparatus, a more detailed diagram of it is given later in Fig. 7.

2. *Calomel Electrodes*

(*a*) *The Preparation of the Materials used in the Calomel Electrodes. Purification of Mercury.*—About thirty pounds of mercury was purified by washing it with 3 per cent. nitric acid for 24 hours in a modified form of Desha's mercury apparatus, illustrated in Fig. 2. In this apparatus three important changes have been made in the form described by Desha. In his apparatus the mercury, descending from the reservoir (*A*), entered a trap and overflowed into the tube

[1] THIS JOURNAL, **41**, 152 (1909).

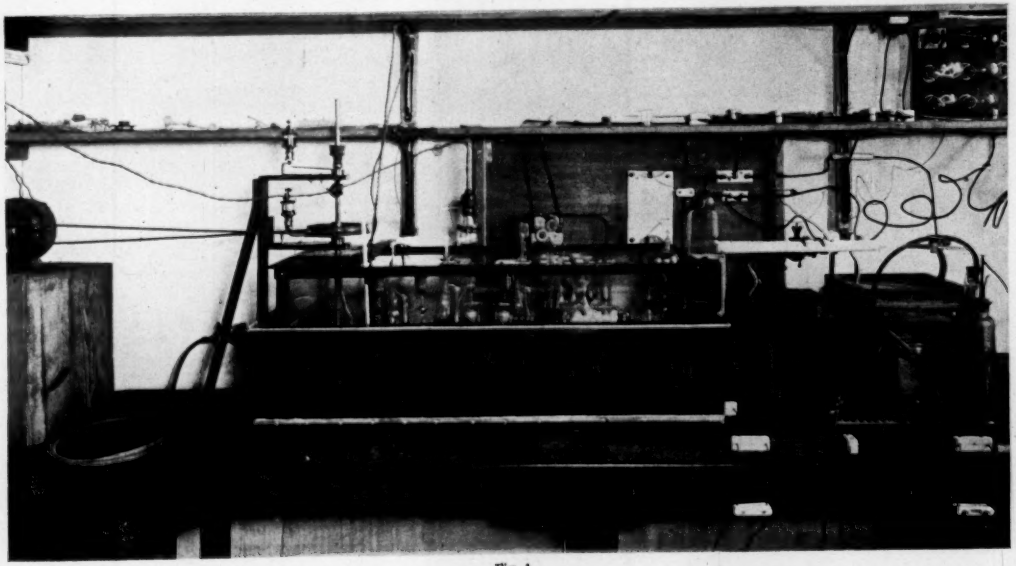

Fig. 1

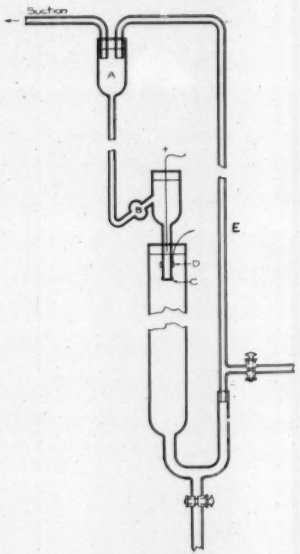

FIGURE 2

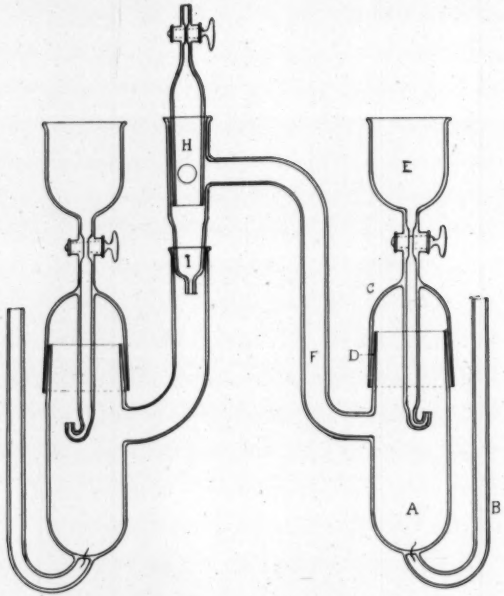

Fig. 3.

leading to the nitric acid. This caused a "dead" space which perhaps slightly decreased the efficiency of the washing. In the apparatus shown in the figure this dead space has been eliminated by the substitution of the bulb (*B*), which keeps all the mercury in circulation. A more important change has been made, however, in the method of spraying the mercury into the acid solution. In Desha's apparatus the mercury streamed through holes in a glass bulb. Hildebrand[1] suggested the use of muslin for spraying mercury into acid. Professor Morse and Dr. W. W. Holland in this laboratory have improved upon muslin by using No. 21 bolting silk, which has an extremely fine mesh. This practice has been incorporated in this apparatus, the silk being tied with silk thread to the glass tube at (*C*).

Another change consists in the substitution of a tube (*E*) of 3 mm. internal diameter for the 1 mm. tube which Desha used to draw the mercury from the bottom to the top of the apparatus. This change doubled the rapidity of washing. With the 1 mm. tube three minutes were required for 100 cc. of mercury to circulate through the apparatus; only one and a half minutes are required with the larger tube. This form of apparatus makes possible the electrolysis of the mercury simultaneously with the washing, the column of mercury above the silk being made the anode and a piece of platinum foil introduced at (*D*) the cathode. The platinum cathode was inclosed in a silk bag to prevent the deposited metal from dropping back into the solution. After being washed about 500 times through nitric acid the mercury was rinsed with water and allowed to stand under concentrated sulphuric acid until used.

The mercury thus purified was distilled four times in a current of air in an electrolytically heated Hulett vacuum still. An attempt was made to determine the relative purity of the different samples of mercury by Hulett's[2] electromotive-force method by using the sample distilled four times as a standard. Although by this method one part of zinc in 10^{10}

[1] J. Am. Chem. Soc., **31**, 933 (1909).
[2] Phys. Rev., **21**, 388 (1905).

parts of mercury can be detected, no difference could be observed between the samples distilled one, two, three and four times, respectively. We understand that no differences can be detected in the electromotive force of standard Weston cells made in the Bureau of Standards from different samples of mercury purified in a manner similar to ours.

Mercury distilled three times was used for the preparation of calomel and in the calomel electrodes.

Preparation of Calomel.—Pure calomel was prepared by dissolving thrice-distilled mercury in redistilled nitric acid, an excess of mercury being present, then pouring this solution into dilute nitric acid and precipitating the mercurous chloride by the addition of hydrochloric acid with constant stirring. The calomel was filtered and washed thoroughly to remove hydrochloric and nitric acids. It was then shaken with successive portions of water for several days in a shaking machine, then with a dilute solution of potassium chloride and finally with a 0.1 N potassium chloride solution made by dissolving 7.456 grams of ignited recrystallized potassium chloride in conductivity water and diluting the solution to one liter. During the entire procedure free mercury was present and the calomel was protected from the light by the use of bottles painted black.

(*b*) *Form of Cell.*—Some preliminary experiments were next carried out to determine the relative value of different forms of cells for use in comparing the hydrogen electrode against the calomel electrode. Four different types were used and the one finally decided upon as most efficient and best meeting our requirements is that shown in Fig. 3. The cell consists of a tube (*A*) about 2 cm. in diameter and 15 cm. high, into the bottom of which is sealed a platinum wire with which contact is made through a side arm (*B*) containing mercury. Over the top of the cell fits a cap (*C*) with a ground-glass joint (*D*). The cap is attached above to a reservoir (*E*), through which liquid can be poured into the cell. The side tube (*F*) is about one cm. in diameter. The stopcock (*H*), in which the side tube of the cell terminates, serves to prevent the diffusion of liquids into the cell; diffusion is still

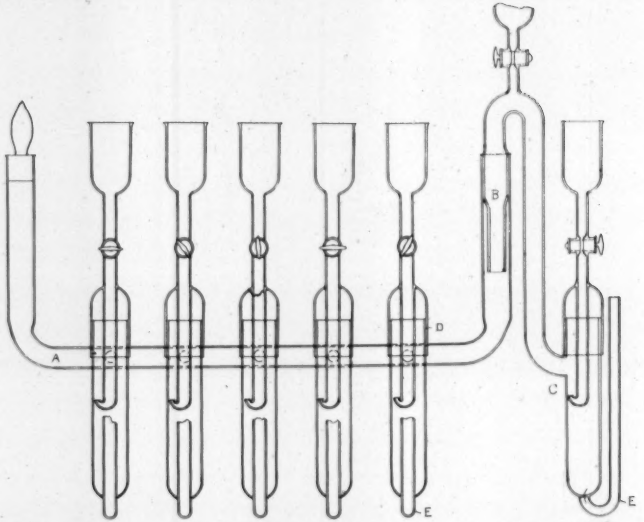

FIGURE 4

more prevented when (*H*) and accessible portions of the wide side tubes are packed with glass or quartz wool. It terminates in the ground joint (*I*) (about 22 mm. long) by which one cell may be connected with another, as shown in the figure, or with the hydrogen electrode apparatus.

The advantages of this form of cell are:

1. The ground-glass cap can readily be removed to allow free access to the inside of the cell for cleaning and filling.

2. The mercury contact through the side arm prevents disturbances of the calomel-mercury paste such as are likely to occur when contact is made by a tube running down inside of the cell.

3. The stopcock and reservoir above the cell permit the rinsing out of the cell with fresh solution when there is any suspicion that impurities have diffused into the side tube.

4. The stopcock at the end of the side tube in a great measure prevents diffusion.

5. The large diameter of the side tube gives a low resistance to the cell.

6. The cell can be immersed entirely in the oil bath, only the reservoirs and stopcocks being above the oil.

This was the form of cell adopted for comparison with the hydrogen electrode. In order that the value used for the potential of the standard electrode might not be dependent upon one electrode only, a battery, Figs. 4 and 4*a*, of ten cells sealed together was prepared, so arranged that the comparison cell could be checked against this battery. These ten cells were of the same type described above except that the side tube was left off and instead five electrodes were sealed to each side of a central tube (*A*). This central tube was turned up at each end and ground to fit the ground joint (*B*) of the electrode (*C*), or (*I*) of the comparison electrode, shown in Fig. 3; the comparison electrode could therefore be directly checked against any of the ten electrodes. Any defective electrode can be emptied, cleaned and refilled at any time without opening the other nine.

(*c*) *Filling the Cells.*—Before the cells were filled they were first cleaned with chromic acid and then washed thoroughly

with water. The platinum wires in the bottom of the cells were coated with mercury by the electrolysis of mercurous nitrate solution. The cells were then filled with a strong solution of potassium hydroxide, allowed to stand 24 hours, washed with water and treated successively with chromic acid, water for 2 days, a solution of potassium hydroxide for 12 hours, dilute nitric acid for 2 hours, water and finally alcohol.

In making up the cells the side arms (*E*) were first filled with mercury, that washed in nitric acid being used for this purpose. About 2 cc. of the mercury distilled 3 times was then placed in the bottom of each cell and on top of this about 4 cc. of the calomel-mercury paste. The apparatus was then filled with a decinormal potassium chloride solution previously saturated with calomel. Recrystallized and ignited potassium chloride and conductivity water were used.

In the earlier experiments thick stopcock grease was used for the ground-glass joint (*D*) between the cap and the cell. The cells were then painted over entirely with a black varnish, especial care being taken to get a good coating of paint over the exposed edge of the ground-glass joint. The paint was intended for the double purpose of protecting the calomel from light and of preventing the oil from dissolving the grease in the ground-glass joint. In spite of this precaution considerable difficulty was at first experienced in the creeping of the oil into the cell. Later this difficulty was obviated by the use of sealing wax in the ground-glass joint. This accomplished the purpose desired but was rather inconvenient to use, as the joint had to be heated upon making up or taking down any cell. There was, furthermore, the attendant danger of cracking the apparatus, which, however, never occurred. Another form of joint has been planned which should obviate this difficulty. It is sketched in Fig. 5. It differs from that shown above in having the cap fit into the top of the cell and in having a mercury trap around the base of the joint at (*A*). Sealing wax will be used to close the ground joint at the exposed edge (*B*).

(*d*) *Measurements with the Calomel Electrodes.*—The battery of calomel electrodes was made up 3 times in all. During

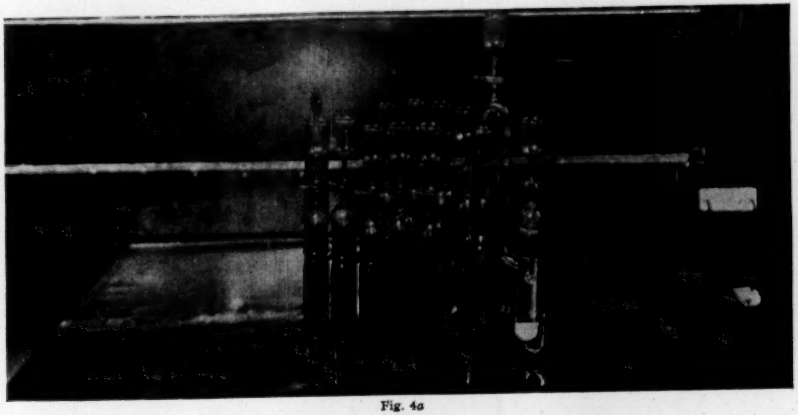

Fig. 4a

the first 2 times difficulty was experienced in keeping the oil out of the cell and individual cells had to be renewed occasionally. The third time sealing wax was used in the joints and this proved efficient in protecting the cell from oil. Only the results of the third series are given in detail. The first 2 series of readings are briefly summarized.

The battery was first made up on November 28, 1910. Four days later the maximum variation of the electrodes was 0.05 millivolt. By December 16, 2 of the 10 electrodes were 0.14 and 0.16 millivolt, respectively, from the mean of the other eight, which differed from each other by a maximum variation of only 0.06 millivolt. These two electrodes were emptied, cleaned out and made up fresh. The potential of these two on December 19 agreed closely with that of the others, there being a maximum variation of 0.10 millivolt. By January 13 the maximum variation had increased to 0.17 millivolt. The battery was taken apart and traces of oil were found in all the electrodes.

The battery was made up a second time on January 24, 1911. On January 26 there was a maximum variation of 0.09 millivolt, which increased to 0.17 by February 10. The caps of the cells were then sealed on with sealing wax. On February 13 the maximum variation was 0.10, which gradually increased to 0.16 by March 7. The battery was then taken apart and cleaned.

On March 9 the battery was made up for the third time and the caps sealed on with sealing wax. In the following tables the calomel electrodes are designated by the numbers 1 to 12. In cleaning the battery Cell No. 6 was accidentally broken and after making up the battery it was found that the potential of No. 7 could not be read because of oil that had crept in between the platinum wire and the mercury in the side tube; only the potentials of 1, 2, 3, 4, 5, 8, 9 and 10 are given. The readings are expressed in hundredths of a millivolt. Cell No. 1 is taken as the standard electrode and considered positive and the potentials of the other electrodes are referred to it. A negative sign before the reading of any electrode means that that electrode is really positive with respect to No. 1.

If, for example, we write No. 1 : No. 9 = +2, No. 9 has a potential of two-hundredths of a millivolt less than No. 1; whereas if we write No. 1 : No. 9 = −2, No. 9 has a potential two-hundredths of a millivolt greater than No. 1.

Date	2	3	4	5	8	9	10
Mar. 10	−11	1	−4	6	−2	−2	−23
11	−5	..	..	9	..	..	−15
13	−4	6	5	7	1	2	−2
14	−3	7	4	7	1	2	−3
15	−3	7	5	7	2	3	−2
16	−2	6	4	6	2	3	0
17	−2	5	4	5	0	0	1
18	−2	5	2	4	0	0	0
20	−5	3	0	1	0	0	1
21	−5	2	1	0	0	−1	0
22	−5	5	0	3	1	1	5
23	−5	5	0	2	0	0	4
24	−5	3	0	0	−4	−1	3
25	−5	3	−3	0	−4	0	3
27	−1	4	−2	0	−2	0	5
29	−1	0	−4	0	−5	0	5
30	−1	0	−6	0	−5	0	4
31	−1	1	−3	4	−2	6	7
Apr. 1	−3	3	−2	4	−3	5	5
3	−2	−1	−7	0	−7	3	4
4	0	0	−4	3	−4	4	6
5	0	0	−5	3	−5	5	5
6	−4	0	−5	2	−6	4	5
7	−5	−3	−7	1	−8	3	5
8	−4	0	−6	1	−8	2	5
10	0	−2	−5	1	−5	5	8
11	0	−4	−5	0	−7	5	4
12	0	−6	−6	1	−6	4	3
13	0	−4	−5	3	−6	6	6
15	0	−2	−4	5	−5	7	8
26	0	0	−5	3	−5	9	10
27	−1	−4	−6	2	−7	6	8

									11 (made up)
	28	—1	—3	—7	1	—8	5	5	—13
May	1	—2	—1	—4	2	—8	5	5	—6
	2	—2	—3	—6	1	—9	5	5	—8
	3	—2	—3	—6	1	—8	5	5	—7
	4	—2	—3	—10	0	—10	2	5	—6
	5	—2	—4	—12	1	—11	3	5	—7
	6	0	—4	—11	1	—10	3	5	—5
	8	0	—1	—9	3	—7	6	10	—1
	9	3	0	—5	4	—4	7	11	0

(*e*) *Conclusions Regarding the Electrodes 0.1 N KCl–HgCl–Hg.*—An examination of this series of readings shows that decinormal calomel electrodes can be prepared which after the first 4 or 5 days will vary from each other by not more than a tenth of a millivolt, the majority being in even much closer agreement. This agreement lasts for about 3 weeks, after which there is a gradual increase in the maximum variation to 0.14 millivolt after 2 months. Essentially the same facts were observed in the first 2 series of readings made when the battery was set up on November 28, 1910, and again on January 24, 1911.

The average constancy of the mean of the seven electrodes is very good. On March 13 the mean potential of the seven was 2.1, on May 9 it was 2.3, when referred to electrode No. 1.

The constancy of the electrodes is shown by their variations from the mean at the beginning and at the end of the experiment:

Date	2	3	4	5	8	9	10	
Mar. 13	—6	4	3	5	—1	0	—4	
May 9	1	—2	—7	2	—6	5	9	
	+7	—6	—10	+3	—5	+5	+13	= Total change

The average change in the potential of the individual electrodes with respect to the mean potential was 0.07 millivolt in 2 months. That a gradual change in the potential of all the cells did not occur is shown by the fact that Cell No. 11, made up on April 27, agreed so closely with the others.

The average daily change in the potential of the electrodes was very nearly 0.01 millivolt, although larger variations often occurred.

Lewis has emphasized the necessity of preparing the calomel-mercury paste for the calomel electrode under uniform conditions. To test the effect of a different sample of calomel, 2 electrodes were made up from calomel prepared about 6 months before that used in the battery. Before use it was shaken out with fresh 0.1 N potassium chloride solution. No difference in the potential of the electrodes due to the change in material could be detected.

A few experiments were made to test the effect of light on the potential of the electrodes. As a rule the cells were painted black, but when left unpainted and exposed to the electric light of the bath and the diffused light of the room no change in potential could be noticed.

3. Experiments upon the Constancy and Accuracy of Reproduction of the Hydrogen Electrode

In the course of the experiments with the hydrogen electrode there were used 19 platinum electrodes designated by the numbers 1 to 19. Of these electrodes three, Nos. 5, 6 and 7, had been prepared by Desha. Nos. 5 and 6 were sheet electrodes of the same style as Nos. 1–4 and 8–19, inclusive. They were made up of sheet platinum, 1 × 2 cm. in size, welded to a piece of platinum wire 1.5 cm. long, which was sealed into the bottom of a glass tube. Contact was made with the electrode by a small quantity of mercury in the bottom of the glass tube. No. 7 was a Cottrell gauze electrode[1] made by weaving together with fine platinum wire the edges of two platinum wire "baskets" from a broken Linneman fractionating column. This gauze sphere was sealed to the end of a piece of glass tubing, through which the hydrogen passed from the washing apparatus. Contact was made with this electrode by a platinum wire running through the tube of the mercury trap of the washing apparatus. Desha had coated the platinum gauze with gold and then with iridium.[2]

[1] Robertson: J. Phys. Chem., **11**, 437. Schmidt and Finger: *Ibid.*, **12**, 406.
[2] Ostwald-Luther, p. 438. Cottrell, Lewis: private communications.

We first used 4 sheet platinum electrodes, Nos. 1–4, inclusive. After the electrodes had been thoroughly cleaned, they were platinized with a solution made of very pure platinum chloride obtained from Heraeus and quite free from iridium and other metals, which often occur in platinum chloride. Electrodes 5, 6, and 7 were also replatinized at this time with the same solution. In platinizing the electrodes no special precautions were used. A potential of 2.5 volts was generally employed and the electrodes adjusted until there was a fairly rapid evolution of gas. The current was commutated each 5 minutes until a good coating of platinum black had been deposited. The behavior of the electrodes appeared to be independent of the thickness of the platinum coating, provided it was so thick that the electrodes did not appear gray.

When platinized, the electrodes were washed with water and then connected 1.5 hours as cathodes in the electrolysis of dilute sulphuric acid. They were finally boiled several hours in water and were then ready for use.

In the earlier experiments the following arrangement was used for comparing the electrodes: Several electrodes were passed through a rubber stopper which fitted the outer jacket of a freezing-point apparatus, and this tube was filled with the acid solution until the electrodes were about three-fourths immersed. The hydrogen was introduced into the solution through a central tube drawn out to a capillary. By this arrangement the hydrogen could not be bubbled directly against the electrodes and hence they were rather slow in coming to equilibrium. The gauze electrode No. 7 could not be compared with the others as its shape prevented its introduction through the rubber stopper. It could be compared with any one of the other electrodes, however, and numerous experiments proved it to have approximately the same potential. These measurements with the gauze electrode are discussed in the next two sections of the experimental work.

In this preliminary work two comparisons of Electrodes 1, 2, 3, 5 and 6 were made. In each case 0.1 N hydrochloric acid was used as the electrolyte. In the first experiment

the electrodes reached a constant potential after 24 hours. Four of the five electrodes showed a maximum variation from each other of 0.08 millivolt. Electrode 1, however, varied by 0.19 millivolt from the mean of the others. It was found to be oily, so it was washed with ether, alcohol and water and then replatinized with pure platinum chloride. After cleaning it thoroughly we compared the electrodes.

In the second comparison the electrodes became constant in potential after 28 hours. The maximum variation between any two was 0.11 millivolt. Four of the five electrodes were within 0.02 millivolt of each other.

Twelve new sheet-electrodes were obtained and were designated by the numbers 8–19. Nos. 8, 9, 12 and 13 were platinized with the pure platinum chloride used for the first electrodes; Nos. 14, 15, 16 and 17 were platinized with ordinary platinum chloride; Nos. 10 and 11 were platinized first with pure platinum chloride and then with the ordinary material, and Nos. 18 and 19 were left bright.

In the comparison of these electrodes another form of apparatus[1] was used. This is shown in Fig. 6. In the actual comparison only one-half of the apparatus was employed. When the second half was used it contained acid of another strength for the comparison of the potentials of the electrodes in acid solutions of two different strengths. The bore of the ground joint (*A*) which joins the two parts of the apparatus was made of the same size as that used in the pair of calomel cells shown in Fig. 3, so that the hydrogen electrodes might be measured directly against a calomel electrode. The large tubes (*B*) had an inner diameter of 2.25 inches and were 6 inches deep. This size enabled us to compare readily 8 or more platinum electrodes (*D*) with each other. The hydrogen bubbled in through the small side tubes (*C*), and escaped through the tube (*E*), which was bent downward at the top to prevent the rapid diffusion of air back into the cell.

[1] We have never noticed any ill effects resulting from the use of rubber stoppers in this cell. It was found to be impossible to construct a glass stopper of this size capable of holding a number of platinum electrodes, but we have now devised another type of apparatus in which the rubber stopper is absent. Comparisons will show whether the rubber stopper is objectionable. We can now compare 34 hydrogen electrodes at once.

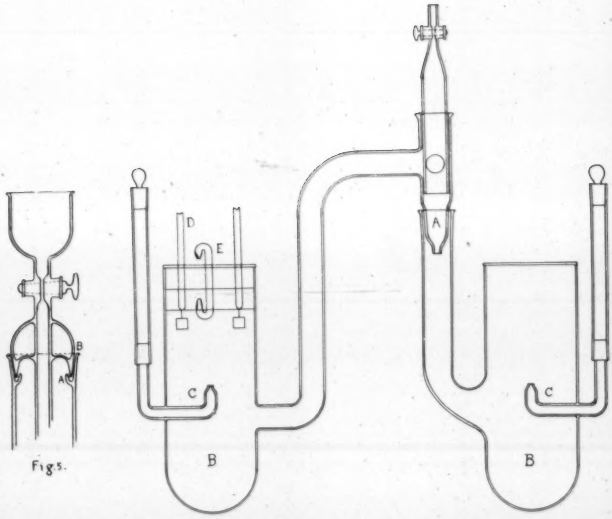

FIGURE 6

Comparison of the Electrodes.—The new electrodes, Nos. 8–17, were not electrolyzed in sulphuric acid before comparison. They were merely washed thoroughly with water and then with alcohol and ether to remove any grease or oil.

In the first experiment Electrodes Nos. 2, 3, 6, 12, 13, 16 and 17 were compared with each other. The detailed measurements are given in the following table. All the electrodes were completely immersed in 0.1 N hydrochloric acid. No. 3 was taken as the comparison electrode and considered positive and the readings with it are given in the same way as in the comparison of the calomel electrodes. The readings are expressed in hundredths of a millivolt:

	Time	2	6	12	13	16	17
May 10,	10.30 A. M.	Started					
	1.00 P. M.	—8	—637	—12	—18	—1	—1
	2.00 P. M.	—4	—272	—9	—13	—1	—3
	4.00 P. M.	—6	—160	—10	—13	1	0
	5.00 P. M.	—6	—109	—9	—10	0	—3
May 11,	9.00 A. M.	—1	—17	—7	—7	1	1
	10.00 A. M.	—1	—10	—5	—5	—1	1

The potentials of six of the seven electrodes show a maximum variation of 0.06 millivolt. The maximum variation of any electrode from the mean of all the electrodes is 0.07 millivolt; the average variation from the mean is 0.03 millivolt.

In the second experiment electrodes Nos. 1, 5, 8, 9, 10, 11, 14 and 15 were compared with each other. No. 5 is taken as the comparison electrode. The data of the experiment are given in the following table:

	Time	1	8	9	10	11	14	15
May 12,	11.50 A. M.	Started						
	1.45 P. M.	—170	—15	—21	—14	6	—347	—75
	2.30 P. M.	—98	—10	—14	5	6	—153	—9
	3.40 P. M.	—36	—4	—4	2	3	—68	—3
	4.40 P. M.	—28	—2	—2	3	3	—52	0
	9.00 P. M.	—2	0	0	—1	0	—8	0
May 13,	9.30 A. M.	—3	0	0	—2	0	—17	—1
	12.30 P. M.	2	2	2	0	1	—2	—2
	3.45 P. M.	3	3	3	3	3	—3	3

The maximum variation between any two electrodes is 0.06 millivolt. The maximum variation of any electrode from the mean of all the electrodes is 0.05 millivolt, and the average variation from the mean is 0.02 millivolt.

In one of the earlier experiments Nos. 3 and 5 were found to have exactly the same potential. We can therefore reduce all the results of the two above tables to the potentials which should be given when electrode No. 3 is compared against any of the electrodes. Considering No. 3 positive, we obtain the figures:[1]

1	2	5	6	8	9	10	11	12	13	14	15	16	17
3	—1	0	—10	3	3	3	3	—5	—5	—3	3	—1	1

The maximum variation of any electrode from the mean is 0.095 millivolt. The mean variation from the mean is 0.030 millivolt. We shall try the experiment of connecting different electrodes as cells, or passing a current through them, to see if the potentials can be made more nearly equal.

The experiments show that the potential of the hydrogen electrode is easily reproduced to within 0.10 millivolt and that the potential which the electrode gives is independent of the purity of the platinum chloride used and the thickness of the coating of platinum black, above a certain limit. To clean the electrode, it need not be used as cathode in the electrolysis of sulphuric acid nor boiled with water; rinsing with ether, alcohol and water is sufficient. The electrodes may be completely immersed in the acid solution into which the hydrogen gas is bubbled.

4. Comparison of the Hydrogen Electrode with the Calomel Electrode

Apparatus and Method of Procedure.—The apparatus used in the comparison of the hydrogen electrode with the calomel electrode is shown in Figs. 7 and 7*a*. The arrangement of the apparatus there is that which was employed when a solu-

[1] In this calculation it is assumed that the relative potentials of Nos. 3 and 5 are constant. This assumption is justified by later experiments in which Electrodes 6 and 7 in different solutions of aniline hydrochloride were found to maintain constant relative potentials. We shall study this point further.

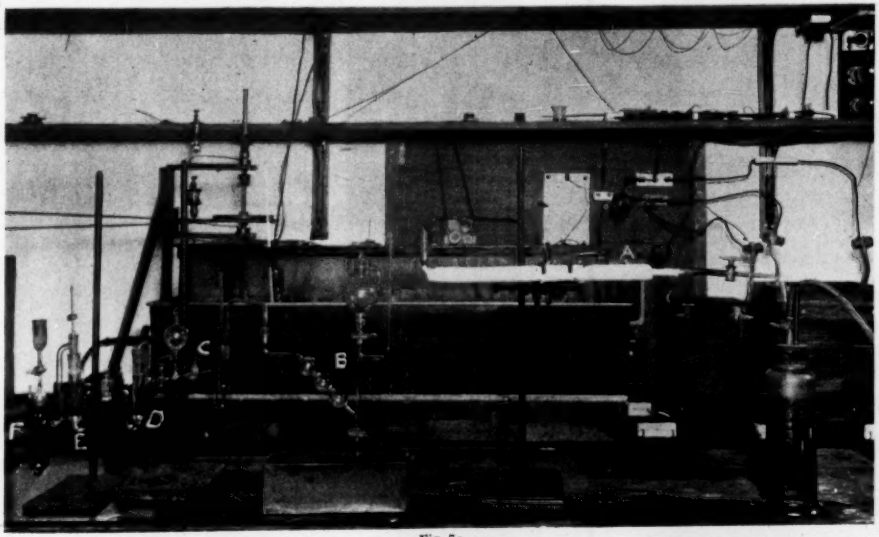

Fig. 7a

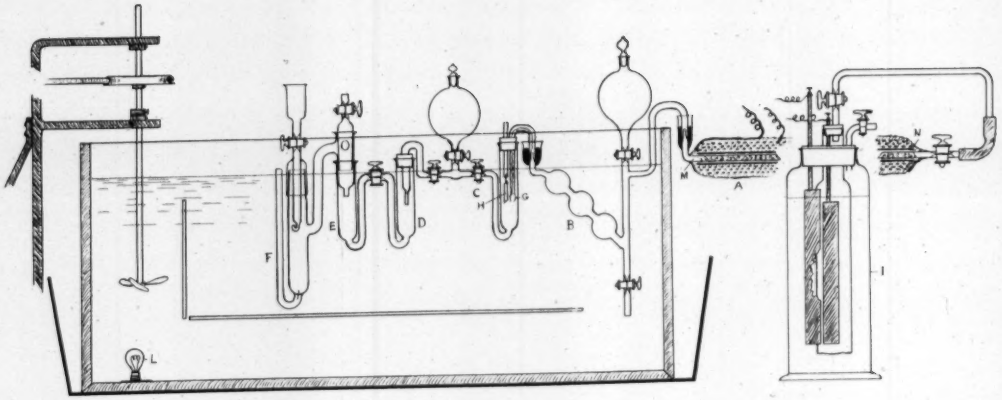

Fig. 7.

tion was used to eliminate the contact potential. The hydrogen passed from the palladium asbestos tube (*A*) through the washing apparatus (*B*) to the gauze electrode (*G*). In most of the experiments a sheet electrode (*H*) was also used, so that one electrode would serve as a check upon the other. The solution in the hydrogen-electrode chamber also filled the rest of the piece of apparatus (*C*). The end of (*C*) dipped into the chamber (*D*) which contained the saturated solution for eliminating contact potential. This solution was prevented from diffusing back into the hydrogen-electrode chamber by the two stopcocks on (*C*). In the chamber (*E*) was placed a 0.1 N solution of potassium chloride, the same as that in the calomel cell (*F*). This solution prevented any diffusion into the calomel electrode of the solution for eliminating contact potential.

In the earlier experiments the hydrogen electrode was compared directly with the calomel electrode without the use of any solution for eliminating contact potential. In such experiments chamber (*D*) served as the hydrogen-electrode chamber and potassium chloride solution was put in (*E*). The piece of apparatus (*C*) was not used. The stopcocks were always closed when measurements were not being made, and often even during measurements. The thin film of solution around the stopper served to conduct the current, although under these conditions the measurements were not quite so accurate. This procedure served to stop diffusion and the attendant changes in potential.

After some preliminary experiments the following method of procedure was adopted: The comparison calomel electrode was first compared with the calomel electrodes of the battery and then placed in position for use with the hydrogen electrode. The objection might be raised to this method of procedure, especially in view of the experience of Coggeshall, that the comparison electrode would change in potential by being moved around. To eliminate any such source of error the comparison calomel cell was again compared with the battery at the completion of the experiment. This was hardly necessary, however, as the following experiment to

test the effect of mechanical disturbance shows. Cell No. 14, one of the comparison electrodes, gave a voltage against No. 7 of the battery of 0.00029 volt. No. 14 was then moved around and put back again with the battery. The voltage of 14 : 7 was 0.00030, a change of only 0.00001 volt. A still more striking proof of the small effect of mechanical disturbance occurred by accident. On February 3, 14 : 7 gave a voltage of 0.00032. On the morning of February 4 No. 14 fell over in the oil bath, flat on its side. It was quickly picked up, the side tube below the stopcock freed from oil (the stopcock was closed at the time of the accident) and immediately compared with No. 7; 14 : 7 gave a reading of 0.00030, a change of only 0.00007 volt being caused by the accident.

The figures just given show the reason for the method of procedure adopted. Whereas the calomel electrodes in the battery were very nearly constant in value, the potential of the comparison electrode fluctuated from day to day, being generally in the neighborhood of two to three-tenths of a millivolt lower in potential than the cells of the battery. This is to be explained by the constant disturbance this cell was subjected to and also to the likelihood of impurities diffusing into the cell during measurements.

Measurement of the Hydrogen Electrode against the Calomel Electrode.—A typical experiment in which the hydrogen electrode was compared with the calomel electrode is given below. The calomel electrode is positive.

An experiment in which two electrodes were used, covering considerably more time, is given on page 609. The gauze electrode, it will be noted, reaches a constant potential much sooner than the sheet electrode. "No. 14" is the calomel electrode, "5" and "gauze" are the two hydrogen electrodes.

The figures given in the seventh column should theoretically be the difference between those in the third and fifth columns. The comparison of the observed and calculated differences shows the accuracy of the measurements.

H_2 — $Pt_{gauze + 5}$ — 0.1 N HCl — 0.1 N KCl — No. 14

14 : 7 = 0.00030

Time Feb. 13	Bar. pres. in ats.	E.M.F. + — 14 : gauze Corr. for calomel elect.	Corr. for bar.	+ — 14 : 5 Corr. for calomel elect.	Corr. for bar.	+ — 5 : gauze Observed	Calculated
9.00 A. M.			Started				
10.50 A. M.	1.003	0.42665		0.42604		0.00058	0.00061
11.33 A. M.		0.42651		0.42594		0.00054	0.00057
12.12 P. M.		0.42650		0.42610		0.00040	0.00040
12.52 P. M.		0.42658	0.42650	0.42618	0.42610	0.00039	0.00040
1.58 P. M.		0.42660	0.42652	0.42624	0.42618	0.00038	0.00036
3.45 P. M.		0.42652	0.42644	0.42634	0.42626	0.00020	0.00018
4.18 P. M.		0.42654	0.42646	0.42645	0.42637	.....	0.00009
4.40 P. M.	1.003	0.42657	0.42649	0.42647	0.42639	0.00009	0.00010
Feb. 14							
8.50 A. M.	1.0044	0.42687[1]	0.42676	0.42673	0.42662	0.00012	0.00014
9.50 A. M.		0.42688	0.42677	0.42680	0.42669	0.00007	0.00008
11.00 A. M.		0.42685	0.42674	0.42678	0.42667	0.00006	0.00007
		Stopped					

14 : 7 = 0.00029

[1] In Baltimore we often have large and sudden fluctuations in the barometric pressure. Since the platinum electrode does not come into equilibrium with the gas instantaneously there is often an uncertainty in the value of the true electromotive force, as is illustrated in this experiment. We have now devised a simple piece of apparatus for keeping the pressure constant at any desired value, and this will be used especially in testing the relation of the electromotive force of the hydrogen electrode to the partial pressure of the hydrogen.

$H_2 - Pt_{No.\,6} - 0.1$ N HCl $- 0.10$ KCl $-$ HgCl $-$ Hg

10 : 14 = 0.00030

Time	E. M. F.
10.30 A. M.	Started
20	0.4050
24	0.4153
56	0.42547
11.12	0.42590
38	0.42610
12.03 P. M.	0.42616
25	0.42619
31	0.42619
37	0.42619
Stopped	
Observed E. M. F.	0.42619
Correction for calomel cell	+0.00030
Barometric pressure,[1] 0.983 ats.; bar. correction	+0.00044
E. M. F.	0.42693

The following table gives the summary of a number of experiments made in this way:

Pt electrode used	Bar. pres. in ats.	E. M. F. observed	E. M F. corrected for for calomel electrode	E. M. F. corrected for bar.
"Gauze"	1.014	0.4265	0.4266	0.42624
No. 5	1.014	0.4261	0.4262	0.42584(?)
No. 3	1.000	0.4265	0.4266	0.42660
No. 2	1.000	0.4263	0.4264	0.42640
No. 4	1.003	0.4266	0.4267	0.42662
No. 1	1.003	0.4262	0.4267	0.42662
No. 6	0.983	0.4262	0.4265	0.42694
No. 6	1.007	0.4266	0.4264	0.42622
"Gauze"	1.009	0.4272	0.4267	0.42647
"Gauze"	1.002	0.4269	0.4266	0.4265
No. 5	0.998	0.4269	0.4266	0.42665
"Gauze"	0.998	0.4270	0.4267	0.42675
"Gauze"	0.998	0.4269	0.4266	0.42665
No. 5	0.998	0.4268	0.4265	0.42655
Average			0.42656	0.42652

[1] The barometric pressure is given in atmospheres; i. e., 760 mm. at 0° C. and 45° latitude. This does not include a correction of about 23.5 mm. for the vapor tension of the solutions at 25°. This correction seems never to have been made by others. The error involved when barometer readings are referred back to 760 mm. partial pressure of hydrogen, as shown by the data presented in this article, is only about 0.00001 volt for the ordinary pressures.

If the very low value 0.42584 is omitted the average is 0.42657, whether the barometer correction is applied or not. If the value 0.42584 is omitted, the mean deviation of the individual readings from the average is 0.00011, and the maximum deviation is 0.00037. As a working average we shall use 0.4266. This is very close to the value 0.4270 found by Bjerrum.

Besides the experiments given above, there were also a few experiments in which values were obtained not agreeing with the others, but in which it was shown that the platinum electrode was at fault.

H_2 — $Pt_{No.\ 1}$ — 0.1 N HCl — 0.1 N KCl — No. 14

10 : 14 = 0.00050

Time	E. M. F.
1.00 P. M.	Started
2.24	0.3666
2.36 P. M.	0.3675
Electrode moved	
2.38 P. M.	0.3666
2.41 P. M.	0.3674
2.44 P. M.	0.3682
2.48 P. M.	0.368
2.55 P. M.	0.3694
Electrode turned around	
3.06 P. M.	0.3659
Experiment stopped	

On inspection the coating of platinum black was found to be very thin. The electrode was replatinized with pure platinum chloride and electrolyzed in sulphuric acid.

We then repeated the above experiment.

H_2 — $Pt_{No.\ 1}$ — 0.1 N HCl — 0.1 N KCl — No. 14

10 : 14 = 0.00047. Bar. pres., 1.003 ats.

Time	E. M. F.	Time	E. M. F.
9.00 A. M.	Started	11.01 A. M.	0.42620
10.08 A. M.	0.42524	11.18 A. M.	0.42630
10.13 A. M	0.42567	11.40 A. M.	0.42615
10.23 A. M.	0.42604	0.42615	= obs. E. M. F.
10.29 A. M.	0.42615	+0.00047	= corr. for No. 14
10.44 A. M.	0.42619	—0.00008	= corr. for bar.
10.52 A. M.	0.42620	0.42654	= corr. E. M. F.

It is seen that the value 0.42654 now given by Electrode No. 1 is in good agreement with the average value of a large number of experiments given above.

In the experimental work dealing with the comparison of the hydrogen electrodes Electrode 4 was broken. In resealing the platinum wire into another piece of glass the platinum black was turned to gray by ignition. This gray electrode was tried in one experiment:

$$H_2 — Pt_{No.\ 4} — 0.1\ N\ HCl — 0.1\ N\ KCl — No.\ 14$$

$$10 : 14 = 0.00014$$

Calomel electrode considered positive

Time	E. M. F.
9.00 A. M.	Started
10.12 P. M	0.00344
10.16 A. M.	0.00280
10.23 A. M.	0.00240
10.48 A. M.	0.00036

Stopped

Electrode 4 was now platinized with ordinary platinum chloride solution, electrolyzed in sulphuric acid, washed with water and again used to check the above experiment. This time a value of 0.4267 was obtained.

Discussion of Results.—In the value 0.42657 of the potential difference measured in these experiments are included three factors, the potential of the calomel electrode, the potential of the hydrogen electrode and the contact potential of the two solutions, decinormal hydrochloric acid and decinormal potassium chloride. For calculating the contact potential of two solutions various formulas have been proposed. The first formula was that of Planck.[1] When applied to two solutions having the same concentration this formula becomes

$$\pi_{25°} = 0.059 \log_{10} \frac{u_1 + v_2}{u_2 + v_1}$$

where u_1, u_2, v_1 and v_2 represent the migration velocities of the anions and cations of the two solutions. Using the data of Kohlrausch and Holborn we obtain at 25° the values

$$H^+ = 352.1,\ K^+ = 74.5,\ \text{and}\ Cl^- = 75.3$$

[1] Wied. Ann., **40**, 561 (1891).

Substituting these data in the equation we obtain 0.0274 as the value of the contact potential at 25°.

There have been various modifications of this formula, for example, that of Henderson[1] and that of Lewis and Sargent.[2] Bjerrum,[3] in a discussion of the accuracy of Planck's and Henderson's formulas, gives 0.0277 as the value of the contact potential between 0.1 N potassium chloride and 0.1 N hydrochloric acid. He also noticed that in the case of some solutions there was a small change in the potential at first, due to diffusion at the planes of contact between the solutions.

Lewis and Sargent's formula has the form

$$\pi = \frac{RT}{F} \log_e \frac{\lambda_1}{\lambda_2}$$

where λ_1 and λ_2 represent the equivalent conductivities of the two solutions. Lewis and Rupert[4] give the values 389.9 for the equivalent conductivity of 0.1 N hydrochloric acid and 128.8 for 0.1 N potassium chloride. These data substituted in the above equation give 0.0284. The same data when applied to Planck's original formula give 0.0266. In the article by Lewis and Sargent 0.0286 is the value given[5] and further evidence for this value is found in the fact that it is identically the same as the value found by Sauer for the potential difference of the combination

$$\text{Hg} - \text{HgCl} - \text{0.1 N KCl} - \text{0.1 N HCl} - \text{HgCl} - \text{Hg}$$

Lewis claims to have ample proof that 0.1 N potassium chloride and 0.1 N hydrochloric acid are equally dissociated (86 per cent.). If the concentration of chlorine ions is the same in each solution, of course the potential of the 0.1 N potassium chloride-calomel electrode will be identical with the potential of the 0.1 N hydrochloric acid-calomel electrode, and the whole

[1] Z. physik. Chem., **59**, 118 (1907); **63**, 325 (1908).

[2] J. Am. Chem. Soc., **31**, 363 (1909).

[3] Z. Elektrochem., **17**, 58 (1911).

[4] J. Am. Chem. Soc., **33**, 306 (1911).

[5] By using the data given by Lewis and Sargent (J. Am. Chem. Soc., **31**, 363) in the footnote on page 365, we calculate the value 0.0293 volt instead of 0.0286 volt given by them at the top of the page. We also find the value 0.0277 volt instead of 0.0271 volt given there.

difference found in comparing the two electrodes will be due to the contact potential.

We thus see that by the use of different data and formulas the calculated values of the contact potential between 0.1 N hydrochloric acid and 0.1 N potassium chloride vary from 0.0266 to 0.0286. As this difference is much greater than is desirable, it was attempted to use some solution to eliminate the contact potential.

Experiments to Determine the Efficiency of Several Solutions for Eliminating Contact Potential.—Following the suggestion of Abegg and Cumming, ammonium nitrate was first used. In these experiments the arrangement of apparatus was that shown in Fig. 7.

The summary of three experiments with the combination

$$H_2 — Pt — 0.1\ N\ HCl — \text{saturated } NH_4NO_3 — 0.1\ N\ KCl — HgCl — Hg$$

is as follows:

Experiment	Bar. pres. in ats.	E. M. F. Corrected for calomel cell	E. M. F. Corrected for bar. pres.
1	0.988	0.3990	0.39931
2	1.009	0.3998	0.39957
3	1.002	0.3995	0.39946
	Average value	0.3994	0.39944

The presence of the saturated ammonium nitrate solution causes a difference in electromotive force of 0.4266—0.3994 = 0.0272.

The requisites of a good salt for eliminating contact potential are that it shall be very soluble and that the velocities of the ions shall be nearly equal. Potassium chloride, while not nearly as soluble as ammonium nitrate, has almost identical velocities for its ions. Saturated ammonium nitrate is about 11 N; saturated potassium chloride at 25°, 4.12 N. The effect of 4.12 N potassium chloride solution was next tried. The following table is a summary of the experiments. Two electrodes were used in each case:

H_2 — Pt — 0.1 N HCl — saturated KCl — 0.1 N KCl — HgCl — Hg

Experiment	Bar. pres. in ats.	E. M. F. Corrected calomel cell	E. M. F. Corrected for bar. pres.
1	1.006	0.4002	0.40005
		0.4002	0.0005
2	1.000	0.4000	0.40000
		0.4000	0.40000
	Average value	0.4001	0.4000

The saturated potassium chloride solution causes a difference of 0.4266 — 0.4000 = 0.0266 volt.

It was impossible to tell from these experiments whether it was better to use potassium chloride or ammonium nitrate, so a series of experiments was run with different concentrations of acids. Here it was possible to calculate the theoretical difference in the electromotive force due to the known change in hydrogen ion concentration. By comparing this theoretical difference with the observed difference, the relative efficiency of different solutions for eliminating contact potential could be determined. Besides ammonium nitrate and potassium chloride, the effect of potassium iodide, potassium bromide and calcium acetate was determined.

In calculating the hydrogen ion concentration of the hydrochloric acid solutions used the following dissociation values were taken:

N HCl	81.0 per cent.	Determined by Sauer
0.1 N HCl	92.2 per cent.	Determined by A. A. Noyes[1]
0.01 N HCl	96.9 per cent.	
0.001 N HCl	100.0 per cent.	

The following table summarizes the results:

[1] The Electrical Conductivity of Aqueous Solutions, Carnegie Institution Publication No. 63, page 141

Contact soln.	Bar. pres. in ats.	HCl conc.	E. M. F. Corrected for calomel electrode	E. M. F. Corrected for barometric pressure	Difference Obs.	Difference Calc.
			0.3364	0.33632		
11 N NH_4NO_3	1.003	1.01 N	0.3368	0.33672		
					0.0632	
					0.0628	0.0576
"	1.003	0.1006	0.3996	0.39952		
					0.0568	0.0578
			0.4566	0.45632		
"	1.011	0.01006	0.4566	0.45632		
					0.0562	0.0582
			0.5126	0.51247		
"	1.005	0.001006	0.5126	0.51247		
			0.3418	0.34208		
4.12 N KCl	0.989	1.01	0.3420	0.34228		
					0.0579	
					0.0577	0.0576
"	1.006	0.1006	0.4001[1]	0.40000		
					0.0579	0.0578
			0.4578	0.45788		
"	0.997	0.01006	0.4578	0.45788		
					0.0582	0.0582
			0.5162	0.51607		
"	1.005	0.001006	0.5162	0.51607		

[1] This is the average of four measurements given on page 615.

TABLE—(*Continued*)

Contact. soln.	Bar. pres. in ats.	HCl conc.	E. M. F. Corrected for calomel electrode	E. M. F. Corrected for barometric pressure	Difference Obs.	Difference Calc.
4.3 N $Ca(O_2CCH_3)_2$	0.998	1.01 N	0.3661	0.36615		
			0.3661	0.36615	0.0712	0.0576
			0.4373	0.43735		
"	0.998	0.1006	0.4373	0.43735		
					0.0664	0.0578
			0.5035	0.50373		
"	0.991	0.01006	0.5035	0.50373		
			0.3940	0.39400		
7.7 N KI	1.000	0.1006	0.3940	0.39400		
					0.0631	0.0578
			0.4571	0.45710		
"	1.000	0.01006	0.4571	0.45710		
					0.0606	
					0.0605	0.0582
			0.5177	0.51770(?)		
"	...	0.001006	0.5176	0.51760(?)		
5.7 N KBr	1.011	0.1006	0.3968	0.39652		
			0.3968	0.39652	0.0606	
					0.0601	0.0578
			0.4568	0.45714		
"	0.987	0.01006	0.4563	0.45664		
					0.0601(?)	0.0582
			0.5166	0.51660(?)		
"	...	0.001006	0.5168	0.51680(?)		

The results given in the above table indicate that potassium chloride is by far the most efficient of the salts used for eliminating contact potential. This conclusion is confirmed by some results obtained with the decinormal hydrochloric acid-calomel electrode.

Potential of H_2—Pt—0.1 N HCl—0.1 N HCl—HgCl—Hg.—Two decinormal hydrochloric acid-calomel electrodes were prepared and measured against the hydrogen electrode in decinormal hydrochloric acid solution. The following corrected values were obtained for the electromotive force of the series

$$H_2 — Pt — 0.1\ N\ HCl — 0.1\ N\ HCl — HgCl — Hg:$$

Bar. pres. in ats.	E. M. F.	E. M. F. corr. for bar. press.
0.994	0.3999	0.40005
0.999	0.4003	0.40006
1.010	0.4005	0.40024
Average	0.4002	0.40012

If we accept Lewis's conclusions that the potential of the 0.1 N HCl — HgCl — Hg electrode is the same as that of the 0.1 N KCl — HgCl — Hg electrode, then the difference between the electromotive force of the element

$$H_2 — Pt — 0.1\ N\ HCl — 0.1\ N\ KCl — HgCl — Hg$$

and that of the element

$$H_2 — Pt — 0.1\ N\ HCl — 0.1\ N\ HCl — HgCl — Hg$$

should be equal to the contact potential of the system 0.1 N HCl — 0.1 N KCl. The actual difference which we find is $0.4266 — 0.4001 = 0.0265$. This value is very close to the difference which we find between the electromotive force of the element

$$H_2 — Pt — 0.1\ N\ HCl — 0.1\ N\ KCl — HgCl — Hg$$

and that of the element

$$H_2 — Pt — 0.1\ N\ HCl — \text{saturated KCl} — 0.1\ N\ KCl — HgCl — Hg$$

viz., $0.4266 — 0.4000 = 0.0266$, the change in potential due to the presence of concentrated potassium chloride solution.

If, therefore, the assumption of Lewis in regard to the iden-

tity in potential of the hydrochloric acid and potassium chloride electrodes is granted, we reach the conclusion from the experiments with the hydrochloric acid electrode, as well as from those in which potassium chloride was used to eliminate contact potential, that *a saturated solution of potassium chloride eliminates almost completely the contact potential of liquid systems, at least those composed of potassium chloride-hydrochloric acid.*

It will be noticed, however, that the acceptance of the above assumption of Lewis also involves the acceptance of the value of 86 per cent. for the dissociation of 0.1 N hydrochloric acid. If this value is used the agreement of the figures obtained for the efficiency of potassium chloride for eliminating contact potential is by no means so good unless a corresponding decrease in the dissociation of the other concentrations of hydrochloric acid is assumed. Inasmuch as the value of 92.2 per cent. for the dissociation of 0.1 N hydrochloric acid is the value generally accepted, this is the value which has been used in calculating the potential of the calomel electrode, but the other values are also discussed.

It should be stated that the values obtained in the experiments involving the hydrochloric acid-calomel electrode are by no means as certain as those with the potassium chloride-calomel electrode, for the reason that only two acid electrodes were prepared. Work is now in progress on the HCl–HgCl–Hg and the H_2SO_4–Hg_2SO_4–Hg electrodes.

Potential of the Decinormal Calomel Electrode

On the assumption that a concentrated solution of potassium chloride entirely eliminates the contact potential of the system 0.1 N HCl — 0.1 N KCl, the value of the electrode 0.1 N KCl–HgCl–Hg becomes 0.4000–0.0591 [—log (0.1006 × 0.922)] = 0.3390. If the dissociation of 0.1 N hydrochloric acid is taken as 86 per cent., the corresponding value of the electrode becomes 0.3372. The value obtained by Sauer is 0.3406. If the contact potential of 0.1 N HCl — 0.1 N KCl is given the value 0.0284 assigned by Lewis, or 0.0286 found by Sauer, experimentally, and 86 per cent. is taken as the

degree of dissociation of 0.1 N hydrochloric acid, the value of the calomel electrode becomes 0.3355. It is evident that we cannot draw final conclusions until we know more accurately the per cent. of ionization of all the electrolytes concerned and have a very accurate method to calculate contact potential, and an experimental method to eliminate it completely. Such measurements of the electromotive force of various systems will perhaps be very helpful in this direction.

In the experiments in the following article the value 0.339 is used as the potential of the system 0.1 N KCl — HgCl — Hg, and the value 0.3355 is compared with this in the discussion.

SUMMARY

This series of experiments has shown that:

1. Calomel electrodes, 0.1 N KCl — HgCl — Hg, can be prepared which for the first three weeks vary not more than 0.10 millivolt. With longer standing the variation slowly increases.

2. Platinum electrodes can be prepared which, when used as hydrogen electrodes in 0.1 N hydrochloric acid, show a variation from the mean value of less than 0.10 millivolt.

3. The electromotive force of the system

$$H_2 — Pt — 0.1\ N\ HCl — 0.1\ N\ KCl — HgCl — Hg$$

is 0.4266.

4. Saturated potassium chloride solution eliminates almost completely the contact potential of systems consisting of potassium chloride and hydrochloric acid.

5. The value of the potential of the electrode 0.1 N KCl—HgCl—Hg is 0.339 if the dissociation of 0.1 N hydrochloric acid is 92.2 per cent.; it is 0.337 if the dissociation of the acid is 86 per cent., and 0.3355 if the contact potential is assumed to be 0.0284. The results obtained by using these different values are discussed in the following article and are found to harmonize better with Lewis's data.

JOHNS HOPKINS UNIVERSITY
BALTIMORE, June 1, 1911

THE APPLICATION OF THE HYDROGEN ELECTRODE TO THE MEASUREMENT OF THE HYDROLYSIS OF ANILINE HYDROCHLORIDE, AND THE IONIZATION OF ACETIC ACID IN THE PRESENCE OF NEUTRAL SALTS

By N. E. Loomis and S. F. Acree

(We are indebted to the Carnegie Institution of Washington for aid in this work.)

We organic chemists have been nearly completely baffled in the study of some of our reactions because of the lack of some *direct, accurate* and *very rapid* method for determining the concentration of hydrogen ions (also hydroxyl, chloride, bromide, sulphide ions) in the presence of all organic compounds, especially when the system is undergoing change.[1] We have methods involving conductivity, catalysis, dilatation, colorimetry, etc., some or all of which can be applied reasonably well in some cases; but all of these methods may fail utterly in special cases, especially when the solution is constantly varying in composition.

When acetamide (or any ester, oxime, etc.) is hydrolyzed in the presence of hydrochloric acid a small amount of the salt of the amide is formed, and the concentration of this salt is constantly diminished as the amide disappears.

$$CH_3CONH_2 + HCl + \overset{+}{H} + \overset{-}{Cl} + CH_3CONH_3Cl + CH_3C\overset{+}{O}NH_3 + H_2O \longrightarrow CH_3COOH + \overset{+}{N}H_4 + \overset{-}{Cl}, \text{ etc.}$$

We have no method to-day for determining the concentrations of the constituents of such a system, as there are too many *unknowns* in the equation. If, however, we had a *direct, accurate, instantaneous method* for determining at any moment the concentration of the hydrogen ions, we could calculate the concentration of the amide salt and its ions, and could then determine directly whether this amide salt, or its ions, or some other constituent, is the substance directly

[1] See the address of the Chairman of the Division of Organic Chemistry in Section C of the American Association for the Advancement of Science, Baltimore, 1908. Science, **30**, 624.

yielding the end products. We have the same case in the decomposition of amides, esters, etc., by alkalis, and just as great a need for a satisfactory method for determining the concentration of hydroxyl ions.

With these facts in mind, and with the advantage of the experiences of Desha[1] in this investigation, we have taken up again the attempt to apply the hydrogen electrode to this problem. In the present communication we are presenting some experiments bearing on the *accuracy of the hydrogen electrode* for determining the concentration of hydrogen ions in the presence of the organic substances aniline and acetic acid. We have chosen these simple compounds because the substances are stable, the constants which we wish to measure have been accurately determined by other methods, and we eliminate the uncertainties due to the changes in a reacting system. The question of the *rapidity* attainable in measuring the concentration of the hydrogen ions of a solution is considered in the next article by Desha and one of us. So many more unforeseen difficulties have beset us in this work with organic compounds than ever occur in work with inorganic substances that we shall present these difficulties rather fully for the benefit of others.

Hydrolysis of Aniline Hydrochloride

One of our first experiments to learn whether the hydrogen electrode might be applied to organic reactions was the determination of the hydrolysis of aniline hydrochloride.

The hydrolysis of this salt had been carefully determined by Bredig[2] by the conductivity method to be 2.63 per cent. at 25° in N/32 solution. Denham had applied the hydrogen electrode to this problem and determined the hydrolysis of aniline hydrochloride in N/16, N/24 and N/32 solutions. For the N/32 solution he obtained the value 2.58 per cent., a result agreeing remarkably well with the value determined by Bredig for the same solution. There are two small points in Denham's work, however, in which there is a chance for difference of opinion. In the first place the number 2.58 is

[1] Desha: Diss., Johns Hopkins Univ., 1909.

[2] Z. physik. Chem., **13**, 289 (1894).

not the percentage hydrolysis of the N/32 solution of aniline hydrochloride, but rather the ratio $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$. To obtain the degree of hydrolysis this value must be divided by 0.96, the degree of dissociation of N/32 hydrochloric acid. This raises the degree of hydrolysis to 2.69. The second point is a much more vital one. He uses the number 0.56 as the value of his normal calomel electrode. This value is the one determined by Rothmund by the drop-electrode method at 18°. Denham's measurements were carried out at 25°. If we apply the temperature factor of the normal calomel electrode as determined by Richards[1] we obtain for the potential of the electrode at 25° the value $0.56 + (7 \times 0.0006) = 0.564$. If this value is used in the calculations instead of 0.56, the ratio $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ for the N/32 solution is found to be 3.02 instead of 2.58, and the per cent. of hydrolysis becomes 3.15, a value differing quite widely from that obtained by Bredig.

Desha attempted to repeat the experiments of Denham, along with other experiments of his own, in this laboratory, but had little success. For the N/32 solution Desha found the ratio $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ to be 5.79. He was troubled chiefly by the decomposition of his material, the solution acquiring a pink color after the experiment had proceeded for a time.

The aniline hydrochloride prepared by Desha had not been recrystallized, whereas the material used by Denham was repeatedly recrystallized from acetone and finally washed with ether. Thinking that the cause of the discrepancies between the results of Denham and Desha might be due to impurities present in Desha's salt, we prepared our aniline hydrochloride with considerable care, especially as Dr. Denham had kindly told one of us of his own difficulties in this connection.

The aniline was fractionally distilled twice, the fraction boiling between 182° and 183° being used for the preparation of the hydrochloride. It was dissolved in ether and the hydrochloride precipitated by passing in dry hydrochloric acid

[1] Z. physik. Chem., **34**, 53 (1897).

gas, the solution being kept cold by an ice bath. The white crystals were filtered off, washed repeatedly with ether and dried over sulphuric acid and caustic potash *in vacuo*. This formed Sample I.

Of this dry salt 4.0478 grams were dissolved in 500 cc. of conductivity water to form a N/16 solution. A portion of this was diluted to form a N/32 solution.

The results obtained with these first two solutions are shown in the following table. In accordance with the practice of both Denham and Desha, saturated ammonium nitrate solution was used to eliminate the contact potential. The value of the calomel electrode used is 0.339.

Concentration	E. M. F. Corrected for calomel electrode	$\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$
N/16	0.5066	2.30
	0.5003	2.95
N/32	0.5124	3.68
	0.4943	7.47
N/32	0.5072	4.51
	0.5064	4.64
N/32	0.5129	3.61
N/32	Indefinite	

As will be noted, the results are extremely discordant. Almost invariably the gauze electrode gave a higher value than the sheet electrode. To see if the electrodes were at fault, they were tested, after the first experiment, in a solution of 0.1 N hydrochloric acid, the electrodes having first been washed with alcohol and ether. Both electrodes gave the same potential, this fact showing that they were all right. It was noted in each of these experiments, after the removal of the electrodes, that there was oil on the surface of the solution. As no trouble of this kind was experienced with solutions of acids, it is probable that the oil was present at first in the aniline hydrochloride, or was the product of the decomposition of some substance present in the aniline hydrochloride solution. As in these experiments it had been the custom to have the sheet electrode partially out of the solution, the lower value of this electrode is probably due to its becoming coated with this oil. In subsequent experiments

the sheet electrode was entirely immersed, but in the other samples of aniline hydrochloride, which were further purified as described below, no traces of oil were found. No pink color, described by Desha, was noticed in the solution in any of the experiments. Constant readings were generally obtained in three hours, the drift being very small after the first hour and a half. A typical experiment with the N/32 solution is given below:

$$H_2 - Pt_{gauze+6} - N/32\ C_6H_5NH_2.HCl - \text{satd. } NH_4NO_3 - \text{0.1 N KCl} - HgCl - Hg$$

Time	Electromotive force 14 : gauze	14 : 6
12.06 P. M.	Started	
12.11 P. M.	0.5021	0.4995
12.55 P. M.	0.5058	0.5042
1.58 P. M.	0.5067	0.5055
2.15 P. M.	0.5067	0.5058
3.10 P. M.	0.5070	0.5062

The remainder of the aniline hydrochloride was further purified by precipitating it from alcohol by the addition of ether. The material was filtered off and washed with ether to remove all traces of alcohol. The salt was dried *in vacuo* over solid caustic potash and sulphuric acid. This material constituted Sample II. The hydrolysis of N/16 and N/32 solutions of this salt was determined as before except that experiments were also performed with potassium chloride solution to eliminate the contact potential. The summary of the results is given in the following tables:

	E. M. F. with NH_4NO_3		E. M. F. with KCl	
Conc.	Corr. for calomel electrode	$\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$	Corr. for calomel electrode	$\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$
N/16	0.5005	2.92		
	0.4999	2.99		
N/16	0.5009	2.88	0.5086	2.13
	0.500)	2.88	0.5095	2.06
N/32	0.5126	3.63	0.5161	(3.18)
	0.512	3.62	0.5168	(3.10)
N/32			0.5189	2.86
			0.5190	2.85

The results obtained in the experiments in which potassium chloride was used to eliminate the contact potential agree much more closely with the results obtained by Bredig and by Denham than do those in which ammonium nitrate was used.

The remainder of the aniline hydrochloride was recrystallized from acetone and the product washed thoroughly with ether. After it was dried, solutions were prepared from this Sample III. Only potassium chloride was used in the contact solution with this sample. The results are summarized below:

		E. M. F. with KCl		
Conc.	Bar. pres. in ats.	Corr.[1] for calomel electrode	Corr. for bar.	$\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$
N/16	1.011	0.5088	0.50852	2.15
		0.5092	0.50892	2.11
N/16	1.002	0.5091	0.50905	2.09
		0.5089	0.50885	2.11
N/32	1.011	0.5184	0.51812	2.94
		0.5190	0.51872	2.88
N/32	1.002	0.5184	0.51835	2.91
		0.5184	0.51835	2.91

The agreement between the results of the two experiments at each concentration is very good in this series and furthermore the results agree well with those obtained with Sample II when potassium chloride was used in the contact solution, if the one experiment be excluded in which the values 3.18 and 3.10 were obtained for the N/32 solution.

A typical experiment in which potassium chloride is used in the contact solution is shown below:

$$H_2 — Pt_{\text{gauze}+6} — N/16\ C_6H_5NH_2.HCl\ (III) — \text{satd. } KCl — 0.1\ N\ KCl — HgCl — Hg\ (\text{No. } 14)$$

Time	14 : gauze	14 : 6	6 : gauze
8.42 A. M	Started		
9.52 A. M.	0.5088	0.5048	
10.13 A. M.	0.5090	0.5072	
10.28 A. M.	0.5090	0.5079	
10.58 A. M.	0.5091	0.5085	0.00051
12.08 P. M.	0.5091	0.5089	0.00017

[1] It is worthy of note that the averages of the electromotive force, and of the per cent. of hydrolysis, per cent. of ionization, and other factors depending upon the electromotive force, are approximately the same for long time periods whether corrected for the barometric pressure or not. The fluctuations of the barometer here in Baltimore are such that the pressure averages close to 760 mm. over long time periods.

A fresh lot of aniline hydrochloride was prepared and was extracted four times with about 200 cc. of boiling acetone. The material remaining was well washed with ether, dried, and used as Sample IV:

		E. M. F. with KCl		
Conc.	Bar. pres. in ats.	Corr. for calomel electrode	Corr. for bar.	$\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$
N/16	0.987	0.5087	0.50904	2.10
		0.5083	0.50864	2.13
N/16	0.989	0.5100	0.51028	1.99
		0.5100	0.51028	1.99
N/16	1.009	0.5103	0.51007	2.01
		0.5100	0.50977	2.04
N/32	0.996	0.5182	0.51830	2.93
		0.5180	0.51810	2.95
N/32	1.009	0.5180	0.51777	2.98
		0.5179	0.51767	2.99

Sample V of the aniline hydrochloride was prepared by recrystallizing some of Sample IV from alcohol by the addition of ether. It gave the following results:

		E. M. F. with KCl		
Conc.	Bar. pres. in ats.	Corr. for calomel electrode	Corr. for bar.	$\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$
N/16	1.009	0.5098	0.50957	2.06
		0.5098	0.50957	2.06
N/16	0.996	0.5086	0.50870	2.13
		0.5094	0.50950	2.06
N/16	0.997	0.5102	0.51028	1.99
		0.5097	0.50978	2.04
N/32	0.988	0.5173	0.51761	3.01
		0.5173	0.51761	3.01
N/32	0.998	0.5177	0.51775	2.99
		0.5177	0.51775	2.99
N/32	0.999	0.5183	0.51832	2.93
		0.5180	0.51802	2.96

Sample VI was prepared by recrystallizing the remaining material of Sample V from alcohol by the addition of ether. The results obtained with this material are given in the following table:

Conc.	Bar. pres. in ats.	E. M. F. with KCl: Corr. for calomel electrode	Corr. for bar.	$\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$
N/16	0.997	0.5096	0.50968	2.05
		0.5092	0.50928	2.09
N/16	0.995	0.5100	0.51013	2.01
		0.5097	0.50983	2.04
N/32	0.995	0.5189	0.51903	2.85
		0.5187	0.51883	2.87
N/32	1.003	0.5188	0.51872	2.88

A summary of the results obtained with the different samples of aniline hydrochloride when potassium chloride was used as the contact solution is given in the following table:

Aniline Hydrochloride

Sample	N/16 $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$	Sample	N/32 $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$
II	2.13	II	(3.18)
	2.06		(3.10)
III	2.15		2.86
	2.11		2.85
	2.09	III	2.94
	2.11		2.88
IV	2.10		2.91
	2.13		2.91
	1.99	IV	2.93
	1.99		2.95
	2.01		2.98
	2.04		2.99
V	2.06	V	3.01
	2.06		3.01
	2.13		2.99
	2.06		2.99
	1.99		
	2.04		2.93
VI	2.05		2.96
	2.09	VI	2.85
	2.01		2.87
	2.04		2.88
	2.07	Average	2.93
	0.08	Max. variation from mean	0.08

Excluding the values in the parentheses, we have the average value of 2.07 for the N/16 solution and 2.93 for the N/32 solution. This gives us the following per cent. of hydrolysis of N/16 and N/32 solutions of aniline hydrochloride if we use 0.944 and 0.960 as the degree of ionization of N/16 and N/32 solutions of hydrochloric acid.

2.07/0.944 = 2.19 per cent. hydrolysis of N/16 aniline hydrochloride.

2.93/0.960 = 3.05 per cent. hydrolysis of N/32 aniline hydrochloride.

$$C_6H_5NH_3Cl \rightleftarrows C_6H_5NH_3^+ + Cl^-$$

The per cent. of ionization of aniline hydrochloride can be calculated from conductivity data given by Bredig.[1] From these data the ionization of N/32 aniline hydrochloride is 86.6 per cent. and by extrapolation the ionization of the N/16 solution is found to be 84.4 per cent.

Let k_w = the ionization constant of water and k_b = the affinity constant of aniline.

$$C_6H_5NH_3^+ \rightleftarrows C_6H_5NH_2 + H^+$$

$$\frac{k_w}{k_b} = \frac{C_{C_6H_5NH_2}C_{H^+}}{C_{C_6H_5NH_3^+}} = \frac{[C_{H^+}]^2}{C_{C_6H_5NH_3^+}}$$

$$C_{C_6H_5NH_3^+} = C_{C_6H_5NH_3Cl} \times \textit{ionization}$$

$$= \frac{(1 - \textit{per cent. hydrolysis}/100) \times \textit{ionization}}{\textit{volume}}$$

$$\therefore \frac{k_w}{k_b} = \frac{[C_{H^+}]^2 \times \textit{volume}}{(1 - \textit{per cent. hydrolysis}/100) \times \textit{ionization}}$$

For $V = 16$

$$\frac{k_w}{k_b} = \frac{(0.0207)^2}{(1 - 0.0219) \times 0.844 \times 16} = 0.0000324$$

For $V = 32$

$$\frac{k_w}{k_b} = \frac{(0.0293)^2}{(1 - 0.0305) \times 0.869 \times 32} = 0.0000318$$

Average value of $k_w/k_b = 0.321 \times 10^{-4}$

Tizard[2] obtained by colorimetric methods the value 0.242 ×

[1] Z. physik. Chem., **13**, 191 (1894).

[2] J. Chem. Soc., **98**, 2492 (1910).

10^{-4} for k_w/k_b while Bredig found 0.24×10^{-4} by his conductivity measurements. Two factors enter into the explanation of the difference between these results. The first point is that Tizard assumes that the hydrochloric acid formed by the hydrolysis of the aniline hydrochloride is entirely dissociated. As was pointed out in the discussion of Denham's work, this assumption is not justifiable. The second factor has to do with the calculation of our results. It was pointed out in the discussion of Denham's work that the value assigned to the potential of the calomel electrode plays a large part in the value found for the hydrogen ion concentration. This indicates that the greatest source of uncertainty in the determination of the hydrolysis of aniline hydrochloride is not in any difficulty in the experimental measurements, as Desha thought, but in the determination of the potential of the calomel electrode. If the value of the decinormal calomel electrode is taken as 0.3362, the figure adopted by Desha, the ratio [*H' conc.*] $\times$ 100/[*total salt*] found for N/16 aniline hydrochloride becomes 1.85 instead of 2.07. If Lewis's value of the contact potential between 0.1 N potassium chloride and 0.1 N hydrochloric acid is adopted, viz., 0.0284, the value of the calomel electrode becomes 0.3355 and the ratio [*H' conc.*] $\times$ 100/[*total salt*] becomes 1.81 for the N/16 and 2.56 for the N/32 solution.

If these values are used

$$k_w/k_b \text{ for N/16} = 0.247 \times 10^{-4}$$
$$k_w/k_b \text{ for N/32} = 0.242 \times 10^{-4}$$

This gives an average of 0.244×10^{-4} for k_w/k_b, which agrees well with the values found by Tizard and Bredig. It should be noted that Bredig used the value 383 for the equivalent conductivity of the hydrochloric acid formed by hydrolysis of the aniline salt, whereas Lewis used 389.9. This makes no appreciable difference in k_w/k_b. Bredig's equivalent conductivity should change with change in concentration according to the isohydric principle. We intend to redetermine all the data needed for such work.

Experiments with Acetic Acid

To test the applicability of the hydrogen electrode to the determination of the concentration of the hydrogen ions in solutions containing weak organic acids, a series of experiments was carried out with acetic acid.

First, two experiments were carried out with 0.5 N acetic acid, with saturated ammonium nitrate as the contact solution.

H_2 — Pt — 0.5 N CH_3COOH — satd. NH_4NO_3 — 0.1 N KCl — No. 14

This series gave the results:

E. M. F. Corr. for calomel electrode	Per cent. dissociation
0.4817	0.764
0.4822	0.748

With 0.25 N acetic acid and ammonium nitrate, the results were as follows:

E. M. F. Corr. for calomel electrode	Per cent. dissociation
0.4908	1.069
0.4905	1.081
0.4905	1.081

With 0.25 N acetic acid and potassium chloride as contact solution, the results were the following:

E. M. F. Corr. for calomel electrode	Per cent. dissociation
0.4930	0.982
0.4927	0.993

The difference of approximately 0.1 between the per cent. of ionization determined with ammonium nitrate and that determined with potassium chloride is evidently due to the change in contact potential in the two systems. Judging from the previously described experiments with potassium chloride, that solution is the better for eliminating contact potential and therefore the per cent. ionization of 0.25 N

acetic acid is probably nearer 0.985 than 1.080. By conductivity measurements White and Jones[1] found at 25° the dissociation of 0.5 N acetic acid to be 0.58 and of 0.25 N acetic acid to be 0.89 (calculated by interpolation).

Effect of Neutral Salts upon the Dissociation of Acetic Acid.—The catalytic action of neutral salts is a problem upon which a great deal of work has been done. The literature of this field and the principal theories have been summarized by Acree.[2] Besides the catalytic action of neutral salts upon the velocity of decomposition of diacetone alcohol by alkalis, cane sugar inversion, etc., work has been done upon the effect of neutral salts on the dissociation of weak acids. In the study of this problem two methods have been used heretofore. The conductivity method has been applied by Arrhenius[3] and the colorimetric method by Brunel and Acree[4] and by Szyszkowski.[5] Arrhenius studied the conductivity of acetic, formic and phosphoric acids in the presence of a number of different salts. He came to the conclusion that the effect of small quantities of neutral salts upon the dissociation of the acids is much greater at the higher dilutions of the acids than at the lower; whereas if the amount of salt added is larger, the effect is nearly proportional to the amount of salt added. The addition of 0.125 N sodium chloride and 0.5 N acetic acid increased the hydrogen ion concentration by 5 per cent. A number of factors enter into conductivity measurements which make these results uncertain. Among these factors are the change in hydration and in viscosity caused by the salt; the possibility of double compounds or complex ions between the salt and acid; the relatively small change in conductivity due to any change in the hydrogen ion concentration compared to the conductivity of the salt added; and other factors.

Szyszkowski based his method upon the change in color of methyl orange in the presence of weak acids caused by the addition of neutral salts. He studied acetic and carbonic

[1] THIS JOURNAL, **44**, 159 (1910).
[2] *Ibid.*, **41**, 457 (1909).
[3] Z. physik. Chem., **1**, 110; **11**, 823; **31**, 197 (1899).
[4] THIS JOURNAL, **38**, 120 (1906).
[5] Z. physik. Chem., **58**, 420 (1907); **63**, 421 (1908); **73**, 269 (1910).

acids, using solutions varying from 0.0022 N to 0.046 N. He interpreted his results to mean that neutral salts greatly increase the hydrogen ion concentration of weak acids. Sodium chloride apparently increased the ionization of acetic acid about 23 times. It should be pointed out, however, that Kurt Meyer and also Hantzsch have shown that some dyes unite with salts and form still more deeply colored double compounds. This tends to throw doubt on the validity of Szyszkowski's conclusions until further evidence to the contrary is presented.

It was believed that the hydrogen electrode would prove serviceable in the study of this problem, and to that end a series of experiments was performed.

In order that the effects of potassium chloride and ammonium nitrate for eliminating contact potential might be compared, each solution of acetic acid was used with both contact solutions. The results are included in the following table: The solutions were prepared by mixing 0.5 N acetic acid with an equal volume of the different solutions of potassium chloride. The concentrations given below are the concentrations after mixing the two solutions. To make the table complete the results obtained with 0.25 N acetic acid alone are included. Only the corrected electromotive force readings are given:

	NH_4NO_3 as contact soln.		KCl as contact soln.	
Solution	E. M. F. corr. for bar.	Dissoc.	E. M. F. corr. for bar.	Dissoc.
0.25 N Acetic	0.49032	1.089	0.49308	0.980
	0.49071	1.073	0.49296	0.980
	0.49071	1.073		
0.25 N Acetic + 0.05 N KCl	0.49152	1.041	0.49276	0.990
	0.49192	1.026		
0.25 N Acetic + 0.1 N KCl	0.49271	0.992	0.49178	1.030
	0.49271	0.992	0.49178	1.030
0.25 N Acetic + 0.5 N KCl	0.49445	0.925	0.48945	1.125
	0.49445	0.925	0.48945	1.125
0.25 N Acetic + 2.06 N KCl	0.49837	0.797	0.48575	1.300
	0.49837	0.797	0.48575	1.300

The results of this series of experiments are uncertain. According to the experiments with ammonium nitrate, the addition of a neutral salt appears to decrease the hydrogen ion concentration; according to the experiments with potassium chloride, the hydrogen ion concentration appears to increase. The difficulty evidently lies in the contact potential of the system. We tried to carry out some experiments in which ammonium nitrate was added to acetic acid, but these were unsuccessful for some reason. Instead of the potential becoming constant within about two hours it would continue to rise, showing a decrease in the hydrogen ion concentration of the solution. This may be due to a reduction of the ammonium nitrate to ammonia by the hydrogen in the presence of platinum black.

If we assume the potassium chloride series of results to be the more accurate, as they have been seen to be in other experiments, then the results are not dissimilar to those obtained by Arrhenius. The addition of 0.1 N potassium chloride to 0.25 N acetic acid increases the hydrogen ion concentration about 4.5 per cent. of the original value. We shall extend this study in several related directions.

SUMMARY

1. If we use 0.339 as the value of the electrode 0.1 N KCl—HgCl—Hg, the hydrolysis of a N/16 solution of aniline hydrochloride is 2.19 per cent. while that of the N/32 solution is 3.05 per cent. If we use 0.3355, calculated from the data of Lewis, as the value of this electrode the hydrolysis becomes 1.81 per cent. for the N/16 and 2.56 per cent. for the N/32 solutions, values which agree excellently with those of Bredig and Tizard. The hydrogen electrode gives us then another instrument for studying these relations between conductivity and hydrolysis accurately, and we shall extend these studies to a large number of other organic salts.

2. The addition of potassium chloride to acetic acid solutions slightly increases the dissociation of the acetic acid.

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June 1, 1911

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ON DIFFICULTIES IN THE USE OF THE HYDROGEN ELECTRODE IN THE MEASUREMENT OF THE CONCENTRATION OF HYDROGEN IONS IN THE PRESENCE OF ORGANIC COMPOUNDS

By L. J. Desha and S. F. Acree

(We are indebted to the Carnegie Institution of Washington for aid in this work.)

When an oxime[1] is formed by the reversible reaction between a carbonyl compound and a salt of hydroxylamine, the total amount of oxime formed is of course equal to the amount of hydroxylamine which disappears. This quantity may be determined in any particular reaction by titration with a standard solution of iodine. But the oxime may exist in solution in three forms, free oxime, oxime salt and oxime cation, and the quantity measured by the method referred to is equal to the sum of these three. When it became highly probable that the oxime cation is one of the substances existing in equilibrium with the ketone (aldehyde, etc.), and hydroxylamine salt a means of determining its concentration was sought.

As direct measurement of the concentration of this oxime cation is out of the question the only feasible method of attack seems to be a differential one involving the determination of the amount of free hydrogen ions which disappear in its formation. That is, the free hydrogen ion concentration at any time may be calculated from the known amount of acid added as catalyzer plus that generated by the reaction

$$R_2CO + NH_2OH.HCl \rightleftarrows R_2C{=}NOH + HCl + H_2O$$

and minus any disappearing in the reaction

$$R_2C{=}NOH + HCl \rightleftarrows R_2C{=}NOH.HCl.$$

Consideration of the various known methods for estimating the hydrogen ion concentration during the reaction, and especially when equilibrium is attained, showed that only two

[1] Lapworth and Barrett: J. Chem. Soc., **91**, 1133; **93**, 85. Johnson, Desha and Acree: This Journal, **38**, 258; **39**, 300. See Desha's Dissertation, Johns Hopkins University, 1908, for further work which will soon be published in This Journal.

seemed likely to give satisfaction under the conditions existing in this case, namely, cane sugar inversion and the potential of the hydrogen electrode. The inversion method for determining the concentration of the hydrogen ions, when the system is at equilibrium, has proven very satisfactory in some experiments that will be described later in another article.

The use of the hydrogen electrode seemed most promising. From the work of Salm,[1] Friedenthal,[2] Salessky,[3] Schmidt and Finger,[4] Robertson[5] and many others, it was apparent that the method may be applied with considerable accuracy to even very dilute solutions of mineral acids. Particularly suggestive, however, was the work of Denham,[6] who measured the hydrolysis of several inorganic salts and of aniline hydrochloride by this method. The latter instance led to the belief that small amounts of organic substances would not materially affect the measurements.

Realizing the great importance which such a method, if perfected, would have not only as regards the problems in hand but also for the study of many other organic reactions, the matter was gone into quite thoroughly. While it may as well be stated at once that no method of general application has been evolved, some of the observations made may be of general interest, and for the benefit of future workers along the same line it seems advisable to give here a full account of the methods employed and the difficulties encountered.

EXPERIMENTAL

The measurements were made very much in the same way as described in the preceding articles. A Leeds and Northrup "type K" potentiometer was used in part of the work and in the other a simple potentiometer consisting of 5 strands of No. 38 manganin wire on a meter slide-wire bridge. The

[1] Z. Elektrochem., **10**, 341, Z. physik. Chem., **87**, 471.
[2] Z. Elektrochem., **10**, 113.
[3] *Ibid.*, **10**, 204.
[4] J. Phys. Chem., **12**, 406.
[5] *Ibid.*, **11**, 437.
[6] J. Chem. Soc., **93**, 41.

wire had a resistance of 50 ohms per meter and proved to be very durable. The two potentiometers were intercompared. The measurements recorded in this article are probably accurate to not more than a millivolt. The hydrogen was made in a Kipp generator by the action of pure sulphuric acid on pure zinc and platinum foil. It was washed well with alkaline solutions and passed over palladium asbestos at 200°–300° to remove the oxygen. The platinum and the gauze iridium electrodes are described in one of the preceding articles.[1] Standard normal and tenth-normal calomel cells were prepared and used as the subsidiary electrodes.

It was desired to measure, if possible, the hydrogen ion concentration of reaction mixtures where such concentration would vary with the time. Calculation of the contact potential between such a solution and the calomel electrode was therefore impracticable. Recourse was had to the use of a saturated solution of ammonium nitrate between the two electrodes. This procedure is stated by Abegg and Cumming[2] to annul the contact potential nearly completely and on this assumption was so used by Denham.[3] That it does not do so entirely is shown by the following data for a cell arranged as follows:

H electrode — HCl — xN NH_4NO_3 (satd.) — 0.1 N KCl — Hg_2Cl_2 — Hg

x	v	dv	dv (calc.)
1.0038	0.3400[4]		
0.10038	0.4018	0.0618	0.0552
0.01	0.4574	0.0556	0.0575
0.001	0.5120	0.0554	0.0586

The normality of the acid used is given under x; under v is the voltage read; under dv is the difference in voltage for two successive concentrations of acid; dv (calc.) is the theo-

[1] THIS JOURNAL, **46**, 602.

[2] Z. Elektrochem., **13**, 17.

[3] *Loc. cit.*

[4] These values, when corrected for the potentiometer, become 0.339, 0.401, 0.456 and 0.511, respectively. Loomis obtained the values 0.3366, 0.3996, 0.4566 and 0.5126 for similar concentrations (THIS JOURNAL, **46**, 616).

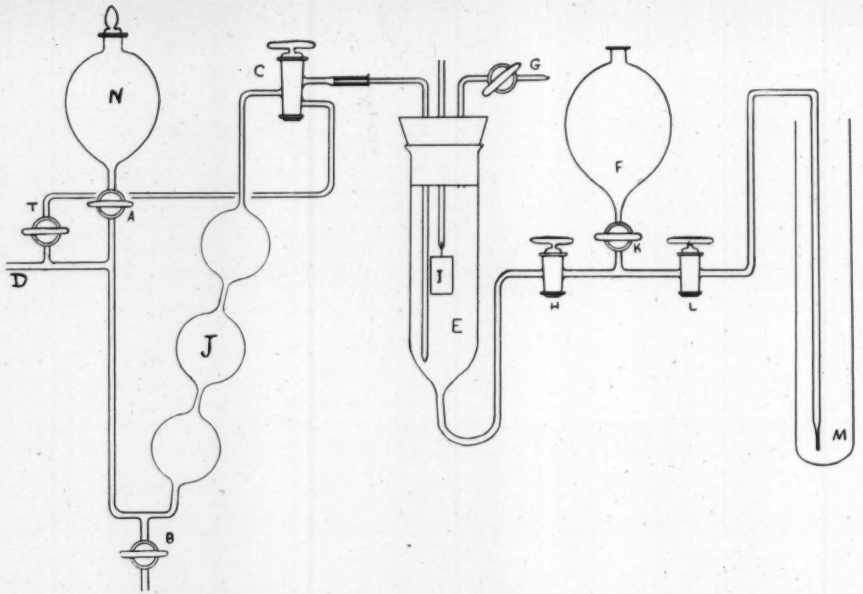

Fig. 1

retical difference in the potentials of two concentrations of acid as calculated from the expression

$$v = 0.0591 \log \frac{c_1}{c_2}$$

(the dissociation of the hydrochloric acid being taken into consideration in computing c_1 and c_2) on the assumption that all contact potential has been eliminated by the ammonium nitrate solution. According to this assumption the values in the third and fourth columns should be identical; the fact is that they are not only different, but one series increases as the other diminishes.[1]

These facts make it impossible to use this expedient in absolute measurements but it is quite possible to apply it (in solutions 0.1 N or more dilute) in the measurement of relative differences in potential, which is all that is desired in work of this kind; for by measuring the potential given by a number of concentrations of acid and plotting the voltage recorded against the known hydrogen ion concentrations, it is possible to obtain a curve which will give accurately the hydrogen ion concentration corresponding to any other voltage read under the same conditions.

One of the first problems which we considered was the study of the *rapidity* with which we may ascertain the true and final value of the electromotive force of a given system. A very rapid determination of the true potential is an absolute necessity if we are to develop a method for measuring, at any moment, the concentration of the hydrogen ions present in reacting systems. Fig. I shows the form of hydrogen electrode and cell used. The pure hydrogen enters at *D*, passes through the washing solution *J* into the glass cell *E*, saturating the hydrogen electrode *I* and passing out at *G*. The calomel

[1] We planned an elaborate series of experiments in which we intended to use potassium chloride, calcium and magnesium acetates, potassium bromide, potassium iodide and other very soluble salts possessing ions moving with nearly the same velocities, but never finished them. Loomis has since studied this question and found that a saturated solution of potassium chloride nearly completely annuls the contact potentials studied (THIS JOURNAL, **46**, 614). We have recently learned that Bjerrum has already done considerable work in this connection (Z. physik. Chem., **83**, 428. Z. Elektrochem., **17**, 389). We shall use saturated solutions of potassium bromide and of potassium iodide with the systems H_2 — Pt — HX — satd. KX — KX — Hg_2X_2 — Hg, in which X is Br or I.

electrode dipping into the saturated solution of ammonium nitrate in *M* completes the hydrogen-calomel cell. The following experiments show how quickly the true electromotive force is established when the solutions are put into the cell and the flow of hydrogen is started. A practically constant potential was registered within ten or fifteen minutes, though a slight drift, amounting to a few tenths of a millivolt, could usually be noticed for one or two hours. As a specimen, the following uncorrected data from an experiment with 0.10038 N hydrochloric acid may be given.

Time	Voltage	Time	Voltage
11.05	(Started)	3.08	(Started)
11.15	0.4011	3.12	0.4018
11.31	0.4013	3.28	0.4020
11.56	0.4015	3.59	0.4018
12.30	0.4020	4.23	0.4018
12.58	0.4017	4.40	0.4018
		5.20	0.4018

The same solution was used in both instances; the current of hydrogen had been discontinued between the two experiments. The same solution was further allowed to remain in the cell in contact with the electrode for two days, no hydrogen being passed in. At the end of that time the hydrogen was turned on and after running for ninety minutes the potential was 0.4019 volt.

Similarly satisfactory results were obtained with 0.01 N hydrochloric acid. When 0.001 N acid was used the high resistance of the solution diminished the sensitiveness of reading. This cell was measured with the Leeds and Northrup "type K" potentiometer.

H electrode — 0.001 N HCl — satd. NH_4NO_3 — 0.1 N KCl — Hg_2Cl_2 — Hg

Time.	Voltage (Started)
11.00 A. M.	0.5095
11.12	0.5080
11.24	0.5075
11.35	0.5100
1.00 P. M.	0.5090
2.10	
Average	0.5088

When solutions contain neutral salts (as would be the case in nearly all reaction mixtures) the conductivity is increased and hence more dilute acids can be read with greater accuracy than here shown.

We then tried some experiments in which we first put the acid solution into F, closed the stopcocks G and L, opened the stopcocks H and K and passed the hydrogen through J, E and F from 30 to 90 minutes in order to saturate the damp platinum electrode I and the acid solution in F before the acid was allowed to flow from F into E and over I. In this way the true electromotive force was established much more quickly, as the following table shows:

[1] t	Volt
6	0.4973
35	0.4975
55	0.4969
74	0.4969
137	0.4964
184	0.4964

Another similar experiment was performed in which an acid solution filling F and E was electrolyzed overnight with I as cathode, a 3-ampere current being used in order to saturate I thoroughly with hydrogen. After changing the solutions in the same way as in the preceding experiment, the following results were obtained:

[1] t	Volt
5	0.4555
11	0.4563
25	0.4563
46	0.4561
130	0.4554

These experiments show that a preliminary saturation of the platinum electrode and the reacting liquid somewhat shortens the time required to obtain equilibrium between the electrode and the solution. After this equilibrium is once established probably no appreciable error will be involved in

[1] t = number of minutes after starting the experiment.

using the observed electromotive force as a measure of the concentration of the hydrogen ions, even when the system is changing.[1]

On the Hydrolysis of Aniline Hydrochloride

After this work was first suggested by one[2] of us, Denham published a very important contribution in which he described the use of the hydrogen electrode in the measurement of the hydrolysis of aniline hydrochloride, his results agreeing very closely with those obtained by Bredig. Denham's results were so valuable that we began to repeat them to see if anyone could readily use the method and to learn the care which must be exercised in this particular work. Instead of preparing the *hydrochloride* in a state of *great purity*, as Denham did, we purified the *aniline* carefully, dissolved it in ether and passed in hydrogen chloride gas. The white precipitate was filtered off, washed with ether and dried over concentrated sulphuric acid and solid potassium hydroxide. An analysis by the silver chloride method showed the salt to be 99.93 per cent. pure. Some solutions were made by dissolving this salt in conductivity water. Others were made by treating weighed quantities of aniline with the required amount of hydrochloric acid. A large number of experiments with various solutions and different electrodes was made but very discordant results were obtained. For instance, a N/16 solution of aniline hydrochloride gave a value 0.4563 at one time and 0.4490 at another time against a normal calomel electrode, Wilsmore having obtained the value 0.4567. Similarly, one platinum electrode in a N/32 solution of aniline hydrochloride gave a value of 0.4662 volt, whereas another electrode gave a value 0.4611, although both electrodes behaved normally in 0.01 N hydrochloric acid. It was shown very definitely, by exposing the electrodes to the air or allowing air to enter the apparatus, that, unless the oxygen is rigidly excluded, oxidation of the aniline takes place in the presence of the

[1] We are now planning a more elaborate and accurate series to test these points more thoroughly.—S. F. A.

[2] Professor Arthur Lapworth has also advocated the use of the hydrogen electrode in this connection.

strongly catalytic spongy platinum of the hydrogen electrode and greatly varying electromotive forces were recorded. Similar changes in the solutions of hydroxylamine and dimethylaniline were also found. In the solution of aniline hydrochloride a pink color was often developed and an oil appeared, probably from aniline remaining in the aniline hydrochloride. The results of all these experiments and of those of Loomis described in the preceding articles have shown us that in order to secure reliable data in the use of this hydrogen electrode we must work with a perfectly pure sample of *aniline hydrochloride* and must rigidly exclude air from the cell. When this was done by Loomis sufficiently reproducible and harmonizing results were obtained. Hoping to minimize any such trouble, we decided to use dimethylaniline hydrochloride, in which the liability to oxidation is less. These solutions were prepared by dissolving a weighed amount of redistilled dimethylaniline in the corresponding measured volume of standard hydrochloric acid and diluting to the strength desired. Repeated experiments with 0.02 N and 0.01 N solutions prepared in this way showed that in every case the potential rose to a maximum value within 15–30 minutes and then began to fall away slowly. If the electrode was not removed, the vessel kept closed and the hydrogen flow uninterrupted, this falling off would usually amount to only 1.5–2 millivolts for even as long a period as eighteen hours. But if the platinum electrode was removed for some time, thus being brought into contact with the air, the highest value obtainable after replacing it was always from 40–120 millivolts less than that recorded in the first instance.

So far only a single platinum-black electrode (designated Pt_1) had been used with the dimethylaniline hydrochloride solution. The effect of a second electrode of the same kind (Pt_2) and of the iridium one (Ir_1) was now investigated. It soon became apparent that each of these three metal electrodes gave a different value. In a solution of 0.02 N dimethylaniline hydrochloride, Ir_1 gave a maximum potential of 0.5316 volt in 27 minutes. It was removed and replaced by Pt_2 in the same solution; in 26 minutes this gave a maximum value of

0.5036 volt, falling off to 0.5028 after 28 minutes more. Ir_1 was then replaced; 0.5276 volt was recorded in 7 minutes, falling off to 0.5256 after remaining 46 minutes longer. Pt_1 was now introduced and gave 0.5120 volt in 13 minutes. Ir_1 was introduced for the third time and gave 0.5158 volt in 17 minutes, only decreasing to 0.5148 after 77 minutes more. Pt_2 gave 0.4882 and finally Pt_1 registered 0.4958. These results are shown in the following table; the first column gives the order in which the electrodes were introduced; under "time" is given the number of minutes between the introduction of the electrode and the reading of the maximum potential in each case.

	Ir_1		Pt_2		Pt_1	
	Time	v	Time	v	Time	v
1	27	0.5316				
2			26	0.5036		
3	5	0.5276				
4					13	0.5120
5	17	0.5158				
6			4	0.4882		
7					9	0.4958

Between the removal of electrode Ir_1 at the close of Experiment 1 and its introduction in Experiment 3, fifty-two minutes had elapsed, during which time the electrode had been kept in a closed vessel containing some of the same 0.02 N dimethylaniline hydrochloride solution saturated with hydrogen. It was therefore in contact with the air only while being transferred from one vessel to the other; the loss in potential here was only 4.0 millivolts (0.5316–0.5276). Between Experiments 3 and 5 it was exposed to the air continuously for 97 minutes; the loss here was 120 millivolts.

The metal electrodes were naturally suspected of occasioning these peculiar results. But when a check experiment was carried out with 0.01 N hydrochloric acid the next day all these quickly reached the same maximum value, differing not more than 0.5 millivolt among themselves. On removing an electrode and leaving it in contact with the air for an hour the same original value was restored within 8 minutes after replacing it and remained constant indefinitely.

Before such results had been obtained with the aniline compounds certain preliminary experiments were carried out with hydroxylamine hydrochloride solutions, preparatory to the oxime work. After some preliminary experiments with a N/32 solution of this salt fairly constant potentials were obtained which indicated hydrolysis amounting to 6.5 to 11.8 per cent., as against 0.74 per cent. found by Winkelblech[1] at the same dilution. The solutions were then analyzed for hydroxylamine by the iodine method. Ten cc. of the original solution required for oxidation 10.40 cc. of a certain solution of iodine; 10 cc. of the same hydroxylamine hydrochloride solution which had been used in an experiment and was in contact with the platinum electrode for 85 minutes required only 7.67 cc. of the same iodine solution. Some of the same stock solution was used in another experiment in which it remained in contact with the electrode for 260 minutes; 10 cc. of it then required only 4.31 cc. of iodine, indicating a decomposition of 58.6 per cent. Bright platinum electrodes produced little or no decomposition but gave low and unsteady potentials. Knowing that tin has little decomposing action on even free hydroxylamine,[2] we attempted to use block-tin plates on which spongy tin was deposited. The potential given by such an electrode was practically independent of the concentration of the acid surrounding it.

Returning to the plated electrodes, we found that by separately saturating the electrode and the solution with hydrogen a very constant value could be obtained within 5 to 10 minutes after bringing them together. In this time there could be little decomposition of the hydroxylamine, and this was still further retarded when free acid was present. In this way a solution of 0.025 N hydroxylamine hydrochloride in 0.0125 N hydrochloric acid gave a potential only 0.5–0.7 millivolt lower than that given by the pure acid of the same concentration. Similarly, a solution 0.025 N with respect to acetone and 0.0125 N with respect to hydrochloric acid gave a potential only 0.3 millivolt lower than the pure acid. But when

[1] Z. physik. Chem., **36**, 546.
[2] Mackay: P. Nova Scotia Inst. Sci., [2] **11**, 324.

both hydroxylamine hydrochloride and acetone were present the results were quite different. In several cases the maximum potential thus obtained indicated a hydrogen ion concentration about double that which was possible if the hydroxylamine and acetoxime hydrochlorides were completely hydrolyzed.

CONCLUSIONS

1. Some organic compounds are decomposed in the presence of the hydrogen electrode, and especially so when oxygen is present, and the electromotive force observed may not in every case correspond to the concentration of the hydrogen ions present.

2. In most experiments the true electromotive force can be ascertained within 30 minutes after starting the hydrogen electrode. If the platinum black is saturated beforehand the electromotive force can be measured within a millivolt in 5 to 10 minutes.

3. Ammonium nitrate does not entirely eliminate contact potential.

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June 1, 1909

REDUCTION OF MERCURIC CHLORIDE BY PHOSPHOROUS ACID AND THE LAW OF MASS ACTION

BY JAMES B. GARNER

My attention has been called to an error in the interpretation of the data obtained by a study of the reaction which occurs between mercuric chloride and phosphorous acid.[1] I have at once recognized the validity of the criticism and will, therefore, in a subsequent number of THIS JOURNAL, resubmit my calculations based upon the experimental data given.

REVIEWS

RADIUMNORMALMASSE UND DEREN VERWENDUNG BEI RADIOAKTIVEN MESSUNGEN. Von E. RUTHERFORD. Deutsch von DR. B. FINKELSTEIN. Mit 3 Abbildungen im Text. Leipzig: Akademische Verlagsgesellschaft m. b. H. pp. 45.

Rutherford, in this brochure, calls attention to the desira-

[1] THIS JOURNAL, **46**, 361.

bility of an international standard, in terms of which the amount of radium present in any substance can be determined. This is important from both the scientific and commercial side. He suggests a form of electroscope which could be used to detect the γ-rays that are shot off from radium. At the radiological congress in Brussels in 1910 the desirability of an international unit was discussed, and a committee was appointed for this purpose. The committee voted unanimously that the one to work out such a unit was Mme. Curie, the discoverer of radium, and she has undertaken the work.

H. C. J.

An Experimental Course of Physical Chemistry. Part I. Statical Experiments. By James Frederick Spencer, D.Sc. (Liverpool), Ph.D. (Breslau), Assistant Lecturer in Chemistry, Bedford College (University of London). London: G. Bell & Sons, Ltd. 1911. pp. xiv + 228. Price, 3s. 6d.

This little volume is a description of physical chemical apparatus together with a list of experiments to be carried out. The apparatus described is not always the newest or best form. Indeed, very far from it. The Beckmann boiling-point apparatus, as sketched on page 102, is to-day of hardly more than historical interest, and it is very difficult to believe that the apparatus for measuring osmotic pressure described on page 94 could give even approximate results.

Again, the surface-tension method of determining the association factor of a liquid is rather difficult as a general laboratory method.

Such minor defects as those referred to above can easily be remedied in subsequent editions. The book, as a whole, is a convenient laboratory guide, and will doubtless prove to be a useful and valuable contribution to the literature of the field which it aims to cover.

H. C. J.

Hydrocarbures, Alcools et Éthers de la Série Grasse. Par P. Carré, Docteur ès sciences, Professeur à l'Écoles de Hautes Études commerciales, Préparateur à l'Institut de Chimie appliquée. Paris: Octave Doin & Fils. pp. xii + 410. Price, Fr. 10.

This volume is one of a series covering chemistry and forming a part of an extensive "encyclopédie scientifique."

The book is divided into six parts: hydrocarbons, their halogen derivatives, alcohols, ethers, ethereal salts of mineral acids, and derivatives of sulphur, selenium and tellurium.

The general properties and methods of preparation of each class or series of compounds are well set forth and special information is added in the case of the more important individual

compounds. A moderate number of references are given to the literature. The treatment is very systematic and quite thorough, considering the scope of the work. The book is inexpensively but neatly gotten up. E. E. R.

ORGANIC CHEMISTRY FOR THE LABORATORY. By W. A. NOYES, PH.D., Professor of Chemistry in the University of Illinois, Urbana, Ill. Second Edition, Revised and Enlarged. Easton, Pa.: The Chemical Publishing Co. 1911. pp. xi + 291. Price, $2.

The first edition of this useful book has been enlarged by the addition of chapters on Analysis of Organic Compounds, on General Operations, on Ethers, on Hydroxy and Ketonic Acids, and on Carbohydrates. Some thirty preparations have been added to the already large number in the first edition. The material has been rearranged to bring it more nearly in accord with the author's well-known text-book, though it may still be used with any other text-book. New tables are given for nitrogen, the latest atomic weight determinations being used. A chapter is given at the end on the examination and identification of organic compounds.

Each chapter is opened with a good general discussion of the properties and various methods of preparation of the class of compounds under consideration, and the student is further aided toward an understanding of the principles involved by well selected references to the literature, inserted at the beginning of the directions for the preparation of each compound.

The preparations given cover a wide field and involve a great variety of operations. In this way assistance is given the advanced worker who may find here methods adapted to almost any use. The directions are clear and sufficient. The book is well gotten up, though some of the drawings leave something to be desired. E. E. R.